Supporting Information

Stereolithographic 3D printing of pure poly(ether-ester) networks from

spirocyclic monomers via cationic ring-opening photopolymerization at high

temperatures

Danijela Kojic,^{a,b} Katharina Ehrmann,^{a,*} Raffael Wolff,^a Yazgan Mete,^a Thomas Koch,^c Jürgen Stampfl,^{b,c} Stefan Baudis,^{a,b} and Robert Liska^a

^a Institute of Applied Synthetic Chemistry, Technische Universität Wien, Vienna, Austria

^b Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, Institute of Applied Synthetic Chemistry, Technische Universität Wien, Vienna, Austria

^c Institute of Materials Science and Technology, Technische Universität Wien, Vienna, Austria

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1 Experimental

1.1 Materials and general methods

The starting materials γ -butyrolactone (Sigma Aldrich), δ -valerolactone (ABCR), ϵ -caprolactone (TCI Europe), butyl glycidyl ether (TCI Europe), phenyl glycidyl ether (Sigma Aldrich) and resorcinol diglycidyl ether DENACOL EX-201 (Nagase ChemteX) were purchased from the respective companies and used without further purification. The bis(4-tert-butylphenyl)iodoniumtetrakis(1,1,1,3,3,3hexafluoro-2-(trifluoromethyl)propan-2-yloxy)photoinitiators aluminate (tBuIAI, Synthon) and Irgacure 290 (BASF) were kindly provided by the respective companies. Boron trifluoride diethyl etherate (TCI Europe) and triethylamine (Sigma Aldrich) were used without further purification. Commercial grade dichloromethane (CH2Cl2, Donau Chemie) was dried using a PureSolv system (Inert). Column chromatography was performed on a Büchi Sepacore Flash System (Büchi pump module C-605, Büchi control unit C-620, Büchi UV-Photometer C-635, Büchi fraction collector C-660), using glass columns packed with aluminum oxide 90 neutral (Carl Roth). NMR-spectra were recorded on a Bruker Avance DRX-400 FT-NMR spectrometer at 400 MHz for 1H- and 101 MHz for 13C-NMR spectra. The signals are reported with their chemical shifts in ppm and fine structure (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sep = septet, m = multiplet). The chemical shifts were referenced by using the respective NMR-solvent [1H: CDCl3 (7.26 ppm), 13C: CDCl3 (77.16 ppm)] as internal reference. HR-MS analysis was performed for literature-unkown monomers dissolved in HPLC-grade acetonitrile (10 µM). Samples were submitted by a HTC PAL system autosampler (CTC Analytics AG), separated by an Agilent 1100/1200 HPLC with binary pumps, degasser, and column thermostat (Agilent Technologies), and analyzed by an Agilent 6230 AJS ESITOF mass spectrometer (Agilent Technologies).

The conversion and GPC analyses were carried out as single measurements.

1.2 Monomer Synthesis

1.2.1 Synthesis of 2-(butoxymethyl)-1,4,6-trioxaspiro[4.4]nonane (5-S)

The synthesis of 2-(butoxymethyl)-1,4,6-trioxaspiro[4.4]nonane (5-S) was carried out according to a literature procedure by Nishida *et al.*¹ A three-necked flask equipped with a dropping funnel was purged with argon. γ -Butyrolactone (6.63 g, 77.1 mmol, 1 eq.) was dissolved in 19.5 mL dry dichloromethane under argon atmosphere and vigorous stirring at 0 °C and 0.3 mL boron trifuoride diethyl etherate (BF₃•Et₂O, 2.5 mmol, 0.033 eq.) were added to the reaction mixture. Afterwards, a solution of 13.25 mL butyl-glycidylether (92.5 mmol, 1.3 equiv.) in 11.5 mL dry dichloromethane was added dropwise to the reaction solution over a period of 30 min at 0° C. Upon addition, the reaction mixture was left to warm up and stirred for five hours at room temperature, whereupon the addition of 0.4 mL triethylamine (2.7 mmol, 0.036 equiv.) followed. The organic phase was washed three times with 25 mL deionized water and dried over sodium sulfate. The solvent was removed *in vacuo* and the obtained crude product was distilled fractionally (119-120°C, 10 mbar) to yield 29% (4.9 g) of the desired compound as colorless liquid.

¹H-NMR (400 MHz, CDCl₃, δ, ppm): *4.31 (m, 1H, C-O-C<u>H</u>-)*, *4*.16 – 3.2 (m, 8H, O-C<u>H</u>₂), 2.49 – 1.84 (m, 4H, -C-C<u>H</u>₂-C<u>H</u>₂-), 1.51 (m, 2H, C<u>H</u>₂-C<u>H</u>₂-CH₂O-), 1.32 (m, 2H, CH₃-C<u>H</u>₂-), 0.86 (s, 3H, C<u>H</u>₃-). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm):129.81, 74.65, 71.84, 67.53, 31.92, 24.57, 19.52, 14.19



1.2.2 Synthesis of 2-(butoxymethyl)-1,4,6-trioxaspiro[4.5]decane (6-S)

The six-membered spiro-orthoester, 2-(butoxymethyl)-1,4,6-trioxaspiro[4.5]decane (6-S), was synthesized in analogy to 5-S with δ -valerolactone (1.74 g, 17.5 mmol, 1 eq.) as starting material. The obtained crude material was distilled fractionally (104°C, 4 mbar) to yield the desired compound. The product was further purified by flash column chromatography on activated alumina using PE:EE 8:1 as mobile phase, whereby 0.96 g (24%) of the liquid product were obtained.

¹**H-NMR (400 MHz, CDCl**₃, **δ**, **ppm):** 4.56–4.23 (m, 1H, C-O-C<u>H</u>), 4.20 – 3.79 (m, 4H, C-O-C<u>H</u>₂-), 3.71 – 3.29 (m, 4H, -C<u>H</u>₂-O-C<u>H</u>₂-), 1.88 – 1.69 (m, 4H, O-C-C<u>H</u>₂,C<u>H</u>₂-CH₂-O-), 1.54 (m, *J* = 7.2, 1.5 Hz, 4H, C- O-CH₂-C<u>H</u>₂-C<u>H</u>₂-), 1.44 – 1.28 (m, 2H, CH₃-C<u>H</u>₂), 0.91 (t, *J* = 7.4 Hz, 3H, C<u>H</u>₃-). ¹³**C-NMR (100 MHz, CDCl**₃, **δ**, **ppm):** 119.84, 74.66, 72.00, 66.86, 65.19, 32.71, 32.14, 25.09, 22.00, 19.73, 14.39

HR-MS (ACN, ESI+, m/z): calcd.: 231.3077 [M+H]⁺; found: 231.3077 [M+H]⁺



Figure S2. ¹H-NMR spectrum (400 MHz, CDCl₃) of the monomer 6-S

1.2.3 Synthesis of 2-(butoxymethyl)-1,4,6-trioxaspiro[4.6]undecane (7-S)

2-(Butoxymethyl)-1,4,6-trioxaspiro[4.6]undecane (7-S) was synthesized in analogy to 5-S ¹with ε-caprolactone (2.28 g, 20.0 mmol, 1 eq.) dissolved in 5 mL dry dichloromethane under argon atmosphere. The crude material was distilled fractionally (121-124°C, 6 mbar) to separate the product from the lactone, whereby 1.03 g of crude material were obtained. The product was purified using flash column chromatography on neutral alumina with PE:EE 9:1 as mobile phase, yielding 0.67 g (14%) of the desired liquid.

¹**H-NMR (400 MHz, CDCl₃, δ, ppm):** 4.41 – 4.16 (m, 1H, C-O-C<u>H</u>-), 4.11 – 3.25 (m, 8H, C<u>H</u>₂-O), 2.04 (dtd, J = 8.8, 4.2, 2.1 Hz, 2H, O-C-C<u>H</u>₂-), 1.68 – 1.42 (m, 8H, O-CH₂-C<u>H</u>₂), 1.29 (ddd, J = 9.6, 7.7, 6.1 Hz, 2H, CH₃-C<u>H</u>₂-), 0.84 (t, J = 7.4 Hz, 3H, C<u>H</u>₃-).,¹³**C-NMR (100 MHz, CDCl**₃, **δ, ppm):** 124.76, 74.69, 71.80, 66.94, 64.71, 37.69, 32.11, 31.18, 29.74, 23.30, 19.71, 14.38.



1.2.4 Synthesis of 2-(phenoxymethyl)-1,4,6-trioxaspiro[4.4]nonane (5P-S)

2-(Phenoxymethyl)-1,4,6-trioxaspiro[4.4]nonane (5P-S) was synthesized following the synthesis procedure for 5-S. 12.9 g (150 mmol, 1 eq.) γ-butyrolactone and 22.5 g (150 mmol, 1 eq.) phenyl glycidyl ether were used as starting materials. After the work-up, the solvent was removed under reduced pressure and the residue was kept in the freezer overnight. 12.49 g colourless crystals were obtained as crude material. After recrystallization from methanol, 11.55 g (33%) of the pure compound were obtained as white crystals.

MP: 72-73°°C (lit: 78-80°C²), ¹**H-NMR (400 MHz, (DMSO-d**₆ δ , **ppm)**: 7.30 (m, 2H, <u>H</u>C=CH-CH, H^{ar}), 6.95 (m, 3H, CH-C<u>H</u>=CH, H^{ar}), 4.52 (m, 1H, -O-C<u>H</u>-), 4.12 - 3.70 (m, 6H, -O-C<u>H</u>₂-), 2.06 (m, 2H, C-C<u>H</u>₂), 1.93 (m, 2H, -C<u>H</u>₂-).¹³**C-NMR (100 MHz, CDCl**₃, δ , **ppm)**: 158.77, 129.80, 121.52, 114.86, 74.02, 69.52, 68.30, 66.80, 33.06, 24.58.



Figure S4. ¹H-NMR spectrum (400 MHz, DMSO-d₆) of the monomer 5P-S

1.2.5 Synthesis of the bifunctional spiro-orthoester bi-S

The bifunctional monomer (bi-S) was synthesized following a literature procedure.³ To a suspension of 20 g resorcinol diglycidyl ether (90.0 mmol, 1 eq.) and 30 g butyrolactone (350 mmol, 3.8 eq.) in 250 mL dry dichloromethane, a solution of 1.0 mL boron trifluoride etherate (7.8 mmol, 0.087 eq.) in 20 g butyrolactone (232 mmol, 2.5 eq.) was added dropwise at 5° C. After 90 minutes, 6 mL triethylamine were added to quench the reaction. The solvent was evaporated *in vacuo* and the residue was stored in the freezer overnight. The crystalline product was collected by filtration, then washed with cold methanol and recrystallized from methanol. 8.89 g (25%) of the desired compound were obtained as white crystals.

MP: 103-105 °C

¹H-NMR (400 MHz, DMSO-d₆, δ, ppm): 7.30 –7.11 (m, 1H, O-C-C<u>H</u>=C-O, H^{ar}), 6.66 – 6.40 (m, 3H, -C<u>H</u>=C<u>H</u>-, aryl),
 4.60 – 4.38 (m, 2H, -C-O-C<u>H</u>-), 4.12 – 3.67 (m, 12H, -O-C<u>H</u>₂), 2.15 – 2.01 (m, 4H, -C<u>H</u>₂-), 1.97 – 1.85 (m, 4H, -C<u>H</u>₂-).
 ¹³C-NMR (100 MHz, CDCl₃, δ, ppm):160.18, 130.23, 129.73, 107.83, 102.17, 74.14, 69.87, 68.62, 67.91, 33.27, 24.78.

Figure S5. ¹H-NMR spectrum (400 MHz, DMSO-d₆) of the monomer bi-S

1.3 Formulation and specimen preparation

Formulations for photo-DSC measurements were prepared with 1 mol% photoacid generator tBul-Al. The formulations were homogenized using a vortex mixer and afterwards heated to 100 °C for 60 s to obtain homogenous mixtures. For photo-DSC studies, all formulations were used directly after preparation. For the (thermo)mechanical measurements, the monomer formulations were cured with 1 wt% of the photoinitiator Irgacure 290 (IC 290) in a silicone mold ($5 \times 2 \times 40 \text{ mm}^3$ for DMTA; dog-bone-shaped samples in accordance with ISO 527 test specimen 5b, total length of 35 mm and a parallel region dimension of $2 \times 2 \times 12 \text{ mm}^3$ for tensile tests) with a Uvitron INTELLI- RAY 600 UV-oven equipped with a 320-500 nm Hg broadband lamp (600 W; UV-A: 125 mW cm⁻²; vis: 125 mW cm⁻²). The light intensity was set to 100% and the formulations were cured for 30 minutes. The silicon molds were placed on a heated plate (120° C) during the curing process. Formulations containing only spiro-orthoesters were subjected to a post-curing step at 120 °C overnight. Formulations containing the bifunctional epoxide were heated to 100° C, homogenized, and cured for five minutes each on the frontside and on the backside of the sample. The cured polymer specimens were ground to obtain uniform specimens with exact dimensions (deviations < $\pm 0.1 \text{ mm}$).

The formulation for 3D-printing *via* Hot Lithography contained the bifunctional epoxide (65 wt%) and the aromatic spiro-orthoester 5P-S (35 wt%) as monomers **(Figure S6).** Additionally, Irgacure 290 (IC 290,1 wt%) was used as photoinitiator, 9,10-dibutoxyanthracene (DBA, 0.1 wt%) as photosensitizer and ethyl-4-(di¬methyl¬amino)¬benzoate

(EDAB, 0.1 wt%) was used as base to reduce overpolymerization. The formulation was prepared in an orange light laboratory in a brown glass vial to avoid light contact. To obtain a homogenous solution, the formulation was homogenized with a vortex mixer and heated to 100 C.

Figure S6. Polymer structure obtained from photopolymerization of 5P-S and CE (A) and components used for the light-exposure test and 3D-printing: bifunctional epoxide CE (65 wt%) and spiro-orthoester 5P-S as monomers (35 wt%); IC 290 (1 wt%) as photoinitiator; 9,10-dibutoxyanthracene (DBA, 0.1 wt%) as photosensitizer and EDAB (0.1 wt%) as base (B).

1.4 Photo-differential scanning calorimetry

Photo-differential scanning calorimetry (photo- DSC) measurements were performed in triplicates on a Netzsch DSC 204 F1 with an autosampler at 25 °C, 70 °C, 90 °C and 110 °C under N₂ atmosphere. For the monomer formulations and their reactivity study, 1 mol% tBul-Al was used as photoinitiator. Photo-DSC analysis of the printing formulations containing a bifunctional epoxide as crosslinker was performed using Irgacure IC 290 as photoinitiator due to its better thermal stability. The formulations ($12 \pm 2 \text{ mg}$) were irradiated twice (2x 300 s) with an Exfo OmniCureTM series 2000 broadband Hg-lamp (cut-off filters 320–500 nm) at the respective temperatures under constant N₂ flow rate (20 mL min^{-1}). The light intensity was set to 45 mW cm⁻² on the surface of the sample, which corresponds to 1.3 W cm⁻² at the tip of the light guide. During the measurement, the heat flow of the polymerization reaction was recorded as a function of time.

The conversion of the monomers was determined via NMR-analysis as a single measurement after the photo-DSC analysis, following the decrease in the proton singal adjacent to the ring substituent (O- CH) according to eq. S I:

$$C = \left(1 - \frac{integral_{DSC}}{integral_{monomer}}\right) * 100$$

C Conversion of the spiro-orthoester after photo-DSC [%]

integral_{DSC} Peak area after the photopolymerization by photo-DSC

integral_{monomer} Peak area of the monomer

An exemplary NMR spectrum indicating the integrated areas is given in Figure S7.

(S I)

Figure S7. Exemplary NMR spectra of 7S before and after photo-DSC analysis indicating the integrated signals utilized in the conversion calculations in equation SI.

1.5 Size exclusion chromatography

To perform size exclusion (SEC) -analysis, the samples were dissolved with THF containing 0.5 mg mL⁻¹ butylated hydroxytoluene (BHT) as flow marker. The concentrations of the sample solutions were in the range of 2 mg mL⁻¹. The solutions were filtered into GPC vials via a PTFE syringe filter and were subsequently analyzed. SEC analysis was performed with a Waters instrument with three columns connected in series (Styragel HR 0.5, Styragel HR 3 and Styragel HR4) and a Waters 2410 RI detector. Molecular weight of the polymers was examined using conventional calibration with polystyrene standards of 375 – 177 000 Da. The program OmniSEC 5.12 from Malvern was used for data analysis. SEC-analysis of the obtained samples was performed as single measurement.

1.6 Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed with an Anton Paar MCR 301 with a CTD 450 oven and an SRF12 measuring system. The polymer specimens were tested in torsion mode with a frequency of 1 Hz and a strain of 0.1%. The temperature was increased from -100 to 200 °C with a heating rate of 2 °C min⁻¹. The storage modulus (G') and loss factor (tan δ) curves were processed with the software Rheoplus/32 V3.40 from Anton Paar. The glass transition temperature (Tg) was obtained from the maximum of the loss factor (tan δ_{max}). Additionally, storage moduli at Tg and at 20 °C were determined.

1.7 Tensile tests

Tensile tests were performed on a Zwick Z050 tensile machine, equipped with a 1 kN load sensor. The samples were strained with a crosshead speed of 5 mm min⁻¹. During the measurement, a stress–strain plot was recorded for analysis. Five specimens were tested for each formulation with satisfactory reproducibility.

1.8 Volumetric shrinkage behaviour

To determine the volumetric shrinkage of the formulations, densities of formulations before and after curing were measured and volumetric shrinkage in % was calculated from Equation 1. The densities of liquid uncured formulations were measured with a pycnometer. Deviations in shrinkage was within 0.05%.

Formulations for density measurements were prepared with 1 wt% photoacid generator IC 290. The formulations were homogenized using a vortex mixer and afterwards heated to 100 °C for 60 s to obtain homogenous mixtures. The formulations were cured in a silicone mold (5 × 2 × 40 mm³) with a Uvitron INTELLI- RAY 600 UV-oven equipped with a 320-500 nm Hg broadband lamp (600 W; UV-A: 125 mW cm⁻²; vis: 125 mW cm⁻²). The light intensity was set to 100% and the formulations containing only spiro-orthoesters were cured for 30 minutes. The silicon molds were placed on a heated plate (120° C) during the curing process. Formulations containing the bifunctional epoxide were heated to 100° C, homogenized, and cured for five minutes each on the frontside and on the backside of the sample. Unfortunately, purely epoxide-containing samples for density measurements could not be obtained with the same curing protocol, as the epoxide CE was too reactive at the set conditions which led to formation of bubbles. The curing conditions were changed and the epoxide was cured for 60 s using 50% light intensity, but formation of bubbles was observed again.

To measure the densities of cured samples, specific gravity determination measurements were conducted with a Sartorius YDK 01-0D specific gravity determination kit. Measurements were conducted in triplicates. Firstly, the weight of the polymer sample in air W(a) was determined. Secondly, the weight of buoyancy G=W(a)-W(fl) was determined by submerging the weighed sample in distilled. From this, the density of the sample could be determined via the equation

$\rho = \frac{W(a)}{0.99983 \cdot G} \cdot \rho(fl) + \rho(a)$

where 0.99983 is a correction term accounting for wire-buoyancy due to increase in water level for a vessel diameter of 76 mm and $\rho(a) = 0.0012$ g cm⁻³ is a correction term for air buoyancy. The density of water $\rho(fl)$ was taken from a table for the accurate temperature of the distilled water. All measures are given in g or g cm⁻³. Air bubbles were avoided during submerging the sample. A minimal amount of soap was added to decrease surface tension and minimalize adhesion of the liquid on the wire.

The obtained density values within the triplicate measurements exhibit very low deviations, i.e. high precision.

Optical microscopy images to determine birefringence were obtained on a a Zeiss Axio Scope.A1 equipped with a Linkam T95-HS heated sample stage. The cured samples were transferred on the glass slide and observed with 5x and 10x magnification. Pictures were taken through a camera inlet on top of the objective and an etched glass scale bar was used to measure the scale of the images. The images were taken for bulk-cured samples containing CE and 0-75 wt% 5P-S. Curing was conducted by heating the formulations to 100° C, homogenizing them, and curing them in a silicone mold (10 x 4 x 15 mm³) for 60 s with a light intensity of 50% each on the frontside and on the backside of the sample. Pure epoxide samples could not be cured under the same curing conditions due to their strong exotherm behaviour during curing.

1.9 Hot Lithography

The 3D-printing of a pyramid was performed on a heated SLA prototype (Caligma 200 UV). The formulations were irradiated with a 375 nm laser with an energy intensity of 2.32 J and at a set layer thickness of 100 μ m. The printing formulation as well as the material vat, the building platform and the recoating unit were heated to 100 °C prior to the printing process. The laser spot on the surface comprises a diameter of 18 μ m and the laser scan speed was set to 200 mm s⁻¹ for the 3D-printing process. Each layer was irradiated twice, whereby the laser beam was scanned over a two-dimensional plane using a galvanometer scanning system.

1.10 Scanning electron microscopy

SEM images were produced using a Zeiss EVO 10 with a SmartSEM software and an Everhart-Thornley Secondary Electron Detector at an accelerating voltage of 17 kV and magnifications between 200 and 600 times. Prior to imaging, the printed object was placed on a conductive carbon pad and was sputtered with a thin Au-layer.

2 Reactivity study: Influence of temperature

Spiro-orthoesters are known to polymerize via double ring-opening (DRO) polymerization at elevated temperatures.⁴ This is an isomerization reaction, which may occur after single ring-opening (SRO) polymerization has already taken place.⁵ To verify the polymerization mechanisms, size exclusion chromatography (SEC) was conducted to determine the molecular weight, dispersity and degree of polymerization, and ¹H- and ¹³C-APT-NMR spectra were recorded before and after photopolymerization to determine conversion and the ratio of single- to double ring opening SRO/DRO (Table S1).

	T [°C]	$\overline{M_n}$ [Da] ^{a)}	Ð [-] ^{a)}	P _n [-] ^{b)}	C [%] ^{c)}	SRO/DRO ^{c)}
	25	690	1.14	3	12	0.77
	70	700	1.25	3	48	0.67
5-S	90	560	1.26	3	56	0.58
	110	560	1.74	3	61	_ d)
	25	400	1.02	2	3	_ e)
	70	860	1.04	4	10	1.7
6-S	90	910	1.20	4	9	1.3
	110	2390	1.35	10	15	1.2
	25	830	1.02	3	34	_ f)
	70	1090	1.02	4	44	_ f)
7-S	90	1200	1.07	5	51	_ f)
	110	1500	1.25	6	65	_ f)

Table S1. Results obtained from the photoreactivity study of 5-S, 6-S and 7-S at different temperatures (25, 70, 90, 110 °C): number average molecular weight ($\overline{M_n}$), molecular weight distribution (\overline{D}), degree of polymerization (P_n), conversion (C), and ratio between single ring opening and double ring opening (SRO/DRO)

^{a)} determined with SEC-analysis utilizing conventional calibration ^{b)} calculated from $(\overline{M_n})^{c)}$ determined with NMR-analysis ^{d)} ratio could not be calculated due to overlapping DRO and OH signals ^{e)} no significant conversion observed ^{f)} ratio could not be calculated because no SRO-signals were detected

Figure S8. GPC traces of polymerized 5-S, 6-S, and 7-S samples at different temperatures

1. Polymerization mode of 5-S

With a conversion of 12% at 25 °C, the ¹H-NMR spectrum of 5-S after polymerization at room temperature is very similar to the monomer spectrum and is therefore not shown here. At 70 °C, the five-membered spiro-orthoester (5-S) polymerizes *via* double ring-opening and is accompanied by backbiting. The broad singlet detected at 2.7 ppm in **Figure S9 B** can be assigned to the OH-groups from the backbiting side reaction. The quaternary carbonyl peak (1) could be detected in ¹³C-APT-NMR (**Figure S10**) spectra at 173 ppm. A second negative signal at 129.7 ppm (**A**) in addition to the quaternary carbon of the monomer at 129.5 ppm (**a**) proves the presence of the single ring-opened adduct. Spectra at 110 °C exhibit the same characteristics. Therefore, NMR-analysis shows that both polymerization modes occur between 70 °C and 110 °C. Signals at 130 and 134 ppm (**ar1, ar2, Figure S10**) originate from decomposition products of the photoinitiator tBul-Al.

Figure S9. A) ¹H-NMR spectrum (400 MHz, CDCl₃) of monomer 5-S, B) ¹H-NMR spectra after photopolymerization of 5-S at 70° C

Figure S10. Relevant part of ¹³C-APT-NMR spectrum (101 MHz, CDCl₃) after photopolymerization of 5-S at 70° C, which proves the occurrence of both polymerization modes, single and double ring-opening

As a result of this detailed NMR-analysis the found polymerization mode of 5-S is a mix of SRO and DRO (Scheme S1).

Scheme S1. Polymerization modes of 5-S resulting in a statistical copolymer

Polymerization mode of 6-S

The least reactive monomer, the six-membered spiro-orthoester (6-S), reached a conversion of 14% at 110 °C. At lower temperatures, lower conversions are achieved, resulting in little difference between the ¹H-NMR spectra at different temperatures. Thus, only the ¹H-NMR and ¹³C-APT-NMR at 110 °C are shown. Residual monomer peaks were observed after photopolymerization in ¹H-NMR spectra at 110 °C (**Figure S11 B**). While these signals cannot be distinct

from product signals in most cases, two new broad signals at 2.3 and 1.7 ppm indicate the presence of protons from the new aliphatic chain, which are adjacent to the remaining ring (**1**, **2**). The broad singlet detected at 2.2 ppm can be assigned to the OH-groups from the backbiting side reaction. ¹³C-APT-spectra revealed that at 110 °C no DRO took place (Figure S12). The corresponding carbonyl peak was absent and additionally monomer carbon signals could be detected. Moderate amounts of SRO polymerization took place (Scheme S2).

Figure S11. A) ¹H-NMR spectrum (400 MHz, CDCl₃) of monomer 6-S, B) ¹H-NMR spectra after photopolymerization of 6-S at 110° C

Figure S12. ¹³C-APT-NMR spectrum (101 MHz, CDCl₃) after photopolymerization of 6-S at 110° C with moderate amounts of SRO

The polymerization mode of 6-S is therefore determined to be SRO in modest yield (Scheme S2).

Scheme S2. Polymerization mode of 6-S

Polymerization mode of 7-S

The seven-membered spiro-orthoester (7-S), polymerized *via* double ring opening already at 25 °C. A carbonyl signal could be detected during ¹³C-APT-NMR. This is linked to the higher ring-strain and the resulting reactivity of sevenmembered spiro-orthoesters. Accompanying SRO polymerization also took place at all temperatures, which was proven by ¹³C-APT NMR (Figure S14 Scheme S3) in analogy to previous analyses. Residual monomer was detected in ¹H-NMR spectra after photopolymerization at 110 °C, which is consistent with a monomer conversion of 65% (Figure **S11)**. The broad singlet evident at 2.5 ppm indicates formation of OH-groups through backbiting reactions. A deuterium exchange experiment confirmed that the signal corresponds to an OH group (**Figure S14**).

Figure S13. A) ¹H-NMR (400 MHz, CDCI₃) spectra of monomer 7-S, B) ¹H-NMR spectra after photopolymerization of 7-S at 110° C

Figure S14. A) ¹H-NMR spectra (400 MHz, $CDCI_{3}/D_{2}O$) of photopolymerized 7-S at 110° C A) before and B) after deuterium exchange to prove that the signal at 2.6 ppm belongs to OHs generated from backbiting reactions

Figure S15. Relevant part of ¹³C-APT-NMR spectrum (101 MHz, $CDCl_3$), which confirms the presence of both polymerization modes during photopolymerization of 7-S at 90° C

The found polymerization mode of 7-S is therefore a mix of SRO and DRO (Scheme S3).

Scheme S3. Polymerization mode of 7-S resulting in a statistical copolymer.

3 Network characterization

3.1 Crosslinking with bifunctional spiro-orthoester

To compare the impact of the monomer composition on the thermomechanical properties, two different systems were investigated. Thereby, the aromatic monofunctional spiro-orthoester 5P-S and the aliphatic monofunctional spiro-orthoester 5-S were chosen to be polymerized with the bifunctional spiro-orthoester bi-S (Figure S15). The content of the bifunctional monomer was chosen as 25, 50 and 65 wt%.

Figure S16. Monomer structures for the investigated polymerization mixtures: mixed aromatic/aliphatic monomer system 5-S/bi-S (50/50 and 35/65) and aromatic monomer system 5P-S/bi-S (75/25; 50/50 and 35/65)

3.1.1 Aromatic/aliphatic spiro-orthoester monomer system

Dynamic mechanical thermal analysis of the aromatic/aliphatic spiro-orthoester monomer system

The polymerization of the aliphatic 5-S with the aromatic crosslinker resulted in highly elastic materials. The storage modulus, which describes the stiffness and the mechanical strength of a material as well as the glass-

transition temperature T_g are in good accordance with theoretical considerations. With increasing crosslinking density, stiffer materials with higher storage moduli and glass transition temperatures were obtained (Figure S17, Table S2).

Figure S17. Storage moduli (G') and loss factor (tan δ) of the specimens obtained from bi-S and 5-S as monomers in varying compositions and cured with 1 wt% IC 290 as photoinitiator

Table S2. Results obtained from the DMTA-measurements of specimens polymerized from bi-S and 5-S in varying amounts with 1 wt% IC 290 as photoinitiator: content of the compounds in the formulation [wt%], glass transition temperature T_g , storage modulus at 20° C G'₂₀, storage modulus at glass-transition temperature G'_{Tg}

bi-S [wt%]	T _g [°C]	G'20 [MPa]	G′ _{⊺g} [MPa]
25	-15	3.8	44.2
50	-4	0.9	11.7
65	23	161.7	117.9

As expected, rubbery cured materials with 25 and 50 wt% crosslinker bi-S have negative $T_{g}s$ and therefore their storage modulus is lower at 20 °C compared to their storage modulus at T_{g} . The polymerized materials containing 65 wt% crosslinker reach a storage modulus of approximately 161 MPa at 20 °C and a similar storage modulus is obtained at T_{g} . Consequently, the glass T_{g} is the highest for these materials and reaches a value of 23 °C (Table S2).

Tensile testing of the aromatic/aliphatic spiro-orthoester monomer system

We were able to perform tensile tests on the test specimens comprised of 50 wt% and 65 wt% crosslinker bi-S **(Table S3, Figure S18 A)**. The test specimens containing 25 wt% crosslinker were extremely thin and too fragile to be measured. It is assumed that a rather high amount of the liquid monofunctional 5-S evaporated during the post-curing process.

As expected after the DMTA-analysis, the elastic and soft polymers exhibit low tensile strength and are not resilient against mechanical stress. Break sets in at approximately 2 MPa, whereby strains of about 30% are reached (**Table S3**). Since the tested specimens do not differ that much in terms of the crosslinker component, the obtained results from the tensile tests are very similar. The tensile toughness U_T was determined as the area under the tensile curve, which is as expected similar for all analyzed specimens (**Figure S18 B**, **Table S3**).

Table S3: Results obtained from tensile testing for materials polymerized from bi-S and 5-S in varying concentrations with 1 wt% IC 290 as photoinitiator: content of the compounds in the formulation [wt%], stress at break σ_B , strain at break ϵ_B , and tensile toughness U_T

bi-S [wt%]	σ _B [MPa]	ε _в [%]	U _T [MJ/(m³) ⁻¹]	
50	2.5 ± 0.3	28.1 ± 1.4	0.39 ± 0.06	
65	2.2 ± 0.3	30.1 ± 6.7	0.41 ± 0.11	

Figure S18. A) Representative tensile testing curves and mean values for stress and strain at break for the specimens and B) toughness of the materials obtained from the cured polymers consisting of monomers bi-S and 5-S in varying compositions and cured with 1 wt% IC 290 as photoinitiator

Figure S19. Tensile testing curves for all specimens obtained from 5-S/bi-S formulations

3.1.2 Purely aromatic spiro-orthoester monomer system

Dynamic mechanical thermal analysis of the purely aromatic monomer system

(Thermo-)mechanical properties of the cured materials were determined with DMTA-, as it was done for the materials with the aliphatic spiro-orthoester. Herein, a more defined curve progression in the glass transition region is noticeable. This is caused by the better homogeneity of the pure aromatic network. The maximum of the loss factor (tan δ) is shifted towards higher temperatures. The combination of the aromatic monofunctional monomer 5P-S with the aromatic bi-S leads to better and stiffer materials, which is also represented by the obtained T_g values (Figure S20, Table S4). With increasing crosslinking density, the storage moduli also increase and reach their highest values at 65 wt% crosslinker content. This finding agrees well with theoretical considerations. The aromatic substituents increase the strength of the polymers when compared to the materials from the mixed monomer system. Nevertheless, relatively soft and flexible materials were obtained after photopolymerization. To calculate the molecular weight between crosslinks (M_c) for our materials equation SII was applied.⁶ As expected, the molecular weight between crosslinks decreases with increasing crosslinker contents.

$$M_c = rac{
ho_{RT}}{G}$$
 SII

where ρ is the density of the polymer, G is the storage modulus in the rubbery plateau (value obtained at T_g + 20°C) and T is the absolute Temperature used for the rubbery plateau.

Figure S20. Storage modulus (G') and loss factor (tan δ) curves of the specimens obtained from monomers bi-S and 5P-S in varying amounts and cured with 1 wt% IC 290 as photoinitiator

Table S4: Results obtained from the DMTA-analysis of specimens polymerized from bi-S and 5P-S in varying amounts with 1 wt% IC 290 as photoinitiator: content of the compounds in the formulation [wt%], glass transition temperature T_{g} , storage modulus at 20 °C G'₂₀, storage modulus at glass-transition temperature G'_{Tg}, and molecular weight between crosslinks M_c calculated from equation SII

bi-S [wt%]	Т _g [°С]	G'20 [MPa]	G'₁g [MPa]	M _c [g mol ⁻¹]
 25	14	1.7	5.5	7130
50	21	21.1	17.0	1036
65	23	88.3	38.3	497

Tensile testing of the purely aromatic spiro-orthoester monomer system

Tensile tests were performed with the specimens containing aromatic spiro-orthoesters. Hereby, materials from all formulations were tested and show the expected trend (Figure S21 A, Table S5). The tensile strength increases with increasing crosslinking density. Consequently, the strain at break decreases with increasing crosslinker content and is the highest for the material with 25 wt% bi-S. The specimens containing 65 wt% bi-S and 35 wt% 5P-S stand out from the obtained results. A remarkable stress of 10 MPa was reached, whereby strain increases early on and strain at break remained quite high with 120%. The aromatic monomer specimens achieve higher strains at break than their aliphatic analogues. The incorporation of the aromatic monomer leads to slightly stiffer materials with increased stress at break. Furthermore, the tensile toughness of the specimens increases with bi-S content and reaches a high value for the specimen of 65 wt% bi-S, suggesting ductile behavior.

In summary, a positive influence of the aromatic monomer on the thermomechanical properties can be seen. Higher T_g values, tensile strength, and remarkable tensile toughness were achieved.

Figure S21. A) Representative tensile testing curves and mean values for stress and strain at break for the specimens and B) toughness of the materials obtained from materials based on the monomers bi-S and 5P-S in varying compositions and cured with 1 wt% IC 290 as photoinitiator

Figure S22. Tensile testing curves for all specimens obtained from 5P-S/bi-S formulations

Table S5: Results obtained from tensile testing for materials polymerized from bi-S and 5P-S in varying concentrations with 1 wt% IC 290 as photoinitiator: content of the compounds in the formulation [wt%], stress at break σ_B , strain at break ϵ_B and tensile toughness U_T

bi-S [wt%]	σ _в [MPa]	ε _в [%]	U⊤ [MJ m-³]	
25	0.1 ± 0.01	108.1 ± 8.9	0.07 ± 0.01	
50	1.3 ± 0.4	60.6 ± 20.3	0.35 ± 0.09	
65	10.2 ± 0.9	94.8 ± 30.5	7.65 ± 0.92	

3.2 Crosslinking with bifunctional epoxide

Before bulk-photopolymerizations of 5P-S with the epoxide CE were performed, the reactivity of the system was tested with photo-DSC analysis. For successful 3D-printing, the conversion of the crosslinking epoxide is a crucial parameter and was determined after photo-DSC analysis. The obtained DSC-signal of 5P-S was not considered in the calculation of the epoxide-conversion as the obtained polymerization heat of 5P-S was within the error margin of the measurement. The required theoretical heat of polymerization of epoxy groups is 80.6 kJ mol⁻¹ per reactive group (determined with bisphenol A diglycidyl ether, BADGE),⁷ thus the calculation of the epoxide conversion followed equation S III.

$C = \frac{\frac{\Delta H * M}{m_i}}{\frac{m_i}{m_{tot}} * \Delta H_0}$		(S III)
С	Conversion of the epoxide after photo-DSC [%]	
ΔΗ	Experimental polymerization heat [J g ⁻¹]	
Μ	Molecular weight of the monomer [252.31 g mol ⁻¹]	
$\frac{m_i}{m_{tot}}$	Ratio of the monomer mass to total mass [-]	
ΔH_0	Theoretical heat of polymerization of monomer [J mol ⁻¹]	

To prove the incorporation of the spiro-orthoester into the polymer network, ATR-IR spectra were recorded before and after photo-DSC analysis (Figure S23 A). In a first attempt, the photopolymerization of 5P-S without CE was investigated. The photopolymerization progress can be followed *vja* the formation of the carbonyl band (~1730 cm⁻¹) and hydroxyl groups (~3100 – 3600 cm⁻¹). Additionally, the decrease of the C-O stretching band at ~ 1070 cm⁻¹ and the peak broadening at ~1000-1300 cm⁻¹ prove the ring-opening polymerization of the spiro-orthoester.⁸ Figure S23 A clearly shows the change of the mentioned bands. Figure S23 B clearly shows the formation of signals, which can be assigned to the new polymer chain. Additionally, the presence of the back-biting reaction is confirmed with signals A-C and the broad singlet at 2.8 ppm.

Figure S23. A) ATR-IR spectra before (black line) and after photopolymerization (red line) of 5P-S and e with 1 wt% IC 290 as photoinitiator. The formation of carbonyl and hydroxy-signals proves ROP of the spiro-orthoester⁸ and B) ¹H-NMR (400 MHz, CDCl₃) spectra after the photopolymerization of 5P-S confirming the formation of γ -butyrolactone and new hydroxyl-groups

The same analysis was conducted for the formulations containing 25, 50 and 65 wt% CE and the spiro-orthoester 5P-S. For a better overview, only the spectra with 25 wt% and 65 wt% are compared here (Figure S24). The epoxide CE contains a carbonyl group and thus, a carbonyl signal is already observed before photopolymerization. Nevertheless, the formation of the hydroxyl band (~3100 – 3600 cm⁻¹) as well as the increase of the carbonyl band (~1730 cm⁻¹) are detectable. Additionally, the decrease of the C-O stretching band at ~1070 cm⁻¹ confirms the SRO of the spiro-orthoester. While the OH stretching band likely coincides with the C-O stretching band, its decreasing intensity with increasing crosslinker content is an undeniable indicator of ROP, since OH would increase the stretching band intensity in analogy to the OH-band at 3100-3600 cm⁻¹. Thus, the overall decrease of the signal at 1070 cm⁻¹ indicates efficient ROP compared to back-biting. The changes in the IR-spectra are more pronounced for the system containing 25 wt% CE and 75 wt% 5P-S due to higher spiro-orthoester content (Figure S25 A). However, they are also visible for the system containing 65 wt% CE and 35 wt% 5P-S and prove the incorporation of the spiro-orthoester into the polymer network (Figure S25 B).

Figure S24. A: ATR-IR spectra before (black line) and after photopolymerization (red line) of materials obtained from formulations containing 25 wt% CE, 75 wt% 5P-S and 1 wt% IC 290 as photoinitiator. B): ATR-IR spectra of materials obtained from formulations containing 65 wt% CE, 35 wt% 5P-S and 1 wt% IC 290 as photoinitiator, where changes are more subtle yet visible. The formation of carbonyl and hydroxy-signals proves ROP of the spiro-orthoester and its incorporation into the polymer network.

Dynamic mechanical thermal analysis of the materials from 5P-S & epoxide CE

To investigate the influence of the epoxy crosslinker on material properties, specimens with 25, 50, and 65 wt% of the rigid CE were prepared and tested thermomechanically. DMTA of specimens containing 25 wt% CE and 75 wt% 5P-S could not be accomplished. The soft test specimens were torn into two pieces before T_g was reached. The obtained results are shown in Table S6.

Table S6: Results obtained from the DMTA-analysis of specimens polymerized from CE and 5P-S in varying amounts with 1 wt% IC 290 as photoinitiator: CE-content [m(CE)], glass transition temperature (T_g), storage modulus at 20° C (G'_{20}), storage modulus at glass-transition temperature (G'_{Tg}) and molecular weight between crosslinks M_c calculated from equation SIII

m(CE) [wt%]	PI [wt%]	T _g [°C]	G'20 [MPa]	Gʻ _{Tg} [MPa]	M₅ [g mol ⁻¹]
50	1	48	242	50	182
65	1	77	1500	128	72

Tensile testing of the materials from 5P-S & epoxide CE

Tensile tests were performed with the prepared specimens to investigate the tensile strength of the mixed epoxide/spiro-orthoester materials with varying composition. A clear trend between stress (σ_B) and strain (ϵ_B) at

break and the epoxide content was observed **(Table S7)**. The tensile strength could be improved with the bifunctional epoxide: Materials could withstand higher mechanical stress before break set in.

Table S7: Results obtained from tensile testing for materials polymerized from CE and 5P-S in varying concentrations with 1 wt% IC 290 as photoinitiator: weight percent of the compounds [wt%], stress at break σ_B , strain at break ϵ_B , tensile toughness U_T

CE [wt%]	σ _B [MPa]	ε _в [%]	U⊤[MJ/(m³) ⁻¹]
25	0.3 ± 0.1	30.3 ± 3.0	0.07 ± 0.01
50	6.7 ± 1.2	15.8 ± 1.8	0.67 ± 0.19
65	23.9 ± 7.6	6.3 ± 1.3	1.44 ± 0.33

Tensile testing of the materials from 5P-S & epoxide CE

Figure S25: Tensile testing curves for all specimens obtained from 5P-S/CE formulations *of the materials from 5P-S & epoxide CE*

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