

Supporting Information for:

Rapid formation of regulated methacrylate

networks yielding tough materials for lithography-

based 3D printing

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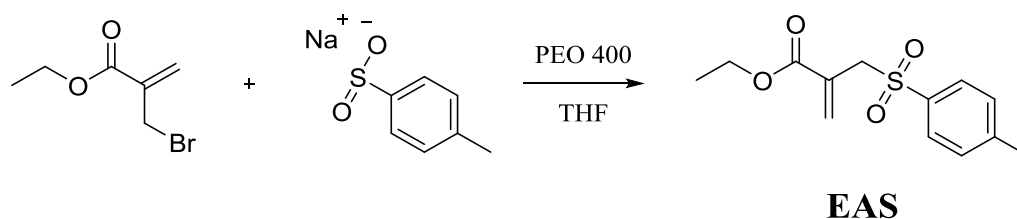
Experimental Section

Materials and Methods

Ethyl pyruvate, p-toluenesulfonyl chloride, sodium p-toluenesulfinate, polyethylene oxide 400, and triethylamine were purchased from Fluka, respectively Sigma-Aldrich. The company Ivoclar Vivadent AG (IVAG) kindly provided the reference monomers 1,10-decanediol dimethacrylate (D3MA), urethane dimethacrylate (UDMA, isomeric mixture; CAS: 72869-86-4), the photoinitiator Ivocerin[®] (bis(4-methoxybenzoyl)diethylgermanium), and the starting material ethyl-2-(bromomethyl)acrylate. A Bruker AC 200 spectrometer was used for NMR experiments (200 MHz for ¹H; 50 MHz for ¹³C) and chemical shifts are reported in ppm using the solvent residual peak (CDCl₃) as reference signal. Multiplicities are referred to as s (singlet), d (doublet), t (triplet), and q (quartet). Coupling constants are given in Hz. Thin layer chromatography (TLC) was performed on TL–aluminum foils coated with silica gel 60 F₂₄₅ (from Merck). For silica gel column chromatography a Büchi MPLC-system equipped with the control unit C-620, fraction collector C-660, and UV-photometer C-635 was used. All reagents and solvents for synthesis were used without further purification unless otherwise mentioned.

Synthesis

Synthesis of Ethyl 2-(tosylmethyl)acrylate (ester activated β-allyl sulfone, EAS)

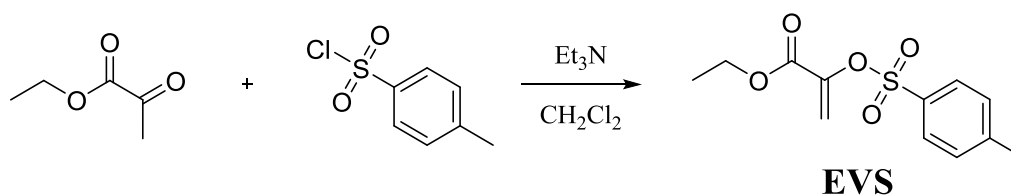


Ethyl 2-(tosylmethyl)acrylate was synthesized according to literature.¹ A 25 mL three-neck round bottom flask was charged with ethyl-2-(bromomethyl)acrylate (1.13 g, 5.84 mmol), sodium p-toluenesulfinate (1.15 g, 6.42 mmol), polyethylene oxide 400 (0.12 g) and dry THF. The reaction was purged with argon, refluxed, and monitored via TLC and ¹H NMR spectroscopy. After approximately 5 hours the reaction was stopped by adding 10 mL deionized water and 10 mL diethyl ether. The aqueous phase was extracted with diethyl ether (3 x 25 mL) and the combined organic phase was then washed with brine (25 mL) and dried over Na₂SO₄. The solution was filtered and the solvent evaporated to yield the crude product. For purification a silica gel column chromatography (petrol ether / ethyl acetate : 2/1) was performed. Overall the reaction gave EAS as a white solid (m.p. 51-52 °C) in 86% theoretical yield.

¹H NMR (200 MHz, CDCl₃, δ, ppm): 7.73 (d, ³J = 8.2 Hz, 2H; Ar-H), 7.32 (d, ³J = 8.2 Hz, 2H; Ar-H), 6.49 (s, 1H; =CH₂), 5.89 (s, 1H; =CH₂), 4.13 (s, 2H; SO₂-CH₂-), 4.02 (q, ³J = 7.2 Hz, 2H; O-CH₂-CH₃), 2.43 (s, 3H; Ar-CH₃), 1.17 (t, ³J = 7.2 Hz, 3H; O-CH₂-CH₃).

¹³C NMR (50 MHz, CDCl₃, δ, ppm): 164.8 (C=O), 144.8 (C4), 135.4 (C4), 133.2 (C2), 129.6 (C3), 129.2 (C4), 128.8 (C3), 61.4 (C2), 57.5 (C2), 21.6 (C1), 14.0 (C1).

Synthesis of Ethyl 2-(tosyloxy)acrylate (ester activated vinyl sulfonate, EVS)



Synthesis of Ethyl 2-(tosyloxy)acrylate is based on a procedure described in literature.² Freshly distilled ethyl pyruvate (5.00 g, 43.1 mmol) was dissolved in 5 mL dry methylene chloride, stirred under argon atmosphere and cooled with an ice bath to approximately 5° C. Triethylamine (4.85 g, 47.8 mmol) was dissolved in 5 mL dry methylene chloride and added drop wise. Solid p-toluenesulfonyl chloride (9.14 g, 47.8 mmol) was added in one shot and the reaction solution diluted with 5 mL dry methylene chloride. The reaction was stirred at ambient temperature until most of the trimethylamine hydrochloride precipitated (approximately 30 min). Another 10 mL dry methylene chloride were added and the reaction mixture was monitored via TLC. After completion, the reaction was quenched with 50 mL deionized water and 50 mL methylene chloride. The organic phase was washed with brine (30 mL), deionized water (2 x 30 mL), and then dried over Na₂SO₄. The crude product was concentrated and additional purification by silica gel column chromatography was performed (petrol ether / ethyl acetate : 3/1). EVS was isolated as pale yellow liquid in 23% theoretical yield.

¹H NMR (200 MHz, CDCl₃, δ, ppm): 7.83 (d, ³J = 8.2 Hz, 2H; Ar-H), 7.34 (d, ³J = 8.2 Hz, 2H; Ar-H), 6.13 (d, ²J = 2.2 Hz, 1H; =CH₂), 5.62 (d, ²J = 2.2 Hz, 1H; =CH₂), 4.14 (q, ³J = 7.2 Hz, 2H; O-CH₂-CH₃), 2.45 (s, 3H; Ar-CH₃), 1.21 (t, ³J = 7.2 Hz, 3H; O-CH₂-CH₃).

¹³C NMR (50 MHz, CDCl₃, δ, ppm): 160.8 (C=O), 145.6 (C4), 143.3 (C4), 132.5 (C4), 129.7 (C3), 128.7 (C3), 116.8 (C2), 61.5 (C2), 21.6 (C1), 13.8 (C1).

Anal. calcd. for C₁₂H₁₄O₅S: C 53.32, H 5.22, S 11.86; found: C 53.49, H 5.23, S 11.57.

Formulations and polymer networks

A reference formulation (A) of equimolar amounts of UDMA and D3MA has been prepared and compared to formulations containing 20 db% (double bond %, meaning that 20% of all double bonds in the resin formulations are AFCT-type double bonds) AFCT reagent (i.e., EAS (B) or EVS (C)). All formulations were mixed together with 1 wt% Ivocerin and placed in an ultra-sonic bath for at least 30 min at ambient temperature. For photo-DSC and real time (RT)-FTIR spectroscopic studies the three formulations were used directly after mixing.

For dynamic mechanical thermal analysis (DMTA) and Dynstat tests all three formulations were poured in silicone molds (5 x 2 x 40 mm³ for DMTA, 10 x 2 x 20 mm³ for Dynstat test). The resins were cured in a Lumamat 100 light oven provided by IVAG. Osram Dulux L Blue lamps were used as irradiation source (18 W, 400-580 nm) and with an Ocean Optics USB 2000+ spectrometer a total intensity of approximately 20 mW cm⁻² was determined at the

position of the silicone molds. All samples were irradiated for 2 x 10 min and flipped in between irradiation periods.

Photo-DSC

For photoreactivity studies a photo-DSC 204 F1 from Netzsch was used. The resins were accurately weighed into an aluminum pan (10 ± 1 mg) and irradiated with filtered light for 5 min (Exfo OmniCureTM series 2000, 400-500 nm, 1 W cm^{-2} measured at the tip of the light guide). An empty pan was used as reference and the polymerizations were conducted at $25 \text{ }^\circ\text{C}$ under inert atmosphere (N_2 flow of 20 mL min^{-1}). The heat flow of the photopolymerization was recorded as a function of time. After the first irradiation period the sample was irradiated for another 5 min to correct the polymerization heat flow by the heat generated from light absorption of the sample.

RT-FTIR measurements

Thin films of all three formulations were prepared on a polyethylene foil with a Mayer rod (number 4) to ensure uniform layer thickness of approximately $10 \text{ }\mu\text{m}$. The films were placed in the sample chamber which was constructed with CaF_2 windows and purged with a constant N_2 flow for RT-FTIR spectroscopic measurements (Fig. S1a). The sample chamber was placed horizontally into a sample holder constructed by Bruker (Fig. S1b). An Exfo OmniCureTM series 2000 with an integrated filter (400-500 nm) and a light guide (3 mm) was used as irradiation source and with an Ocean Optics USB 2000+ Spectrometer the light intensity at the sample position was measured to be 15 mW cm^{-2} . At the beginning of each measurement the recording of the FTIR spectra was started and the light source was turned on with a 5 s delay. Before and during irradiation FTIR spectra of the films were recorded with an approximate frequency of 2 s^{-1} . The area of the double bond peak at $\sim 1638 \text{ cm}^{-1}$ was used to calculate the double bond conversion (DBC) of the cured films. Measurements were performed in duplicate to check reproducibility.

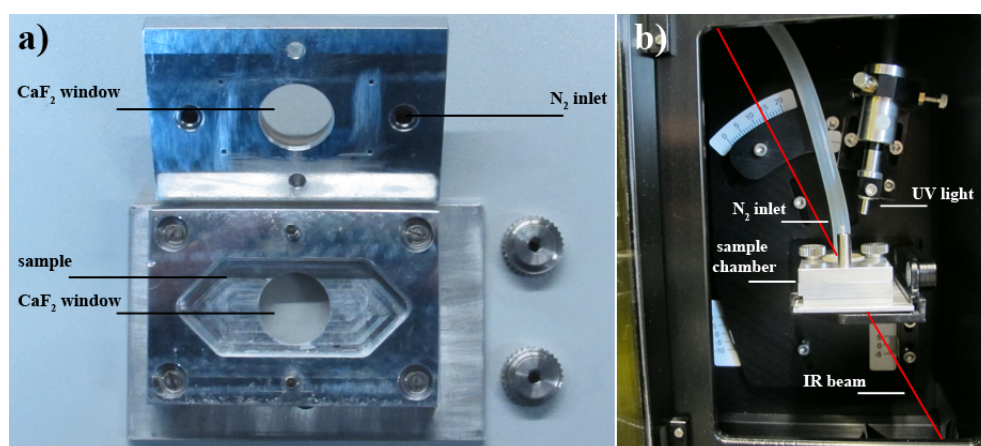


Fig. S1 Sample chamber with CaF_2 windows (a) and RT-FTIR set up (b).

Photorheology

An Anton Paar MCR 302 WESP rheometer with a P-PTD 200/GL Peltier glass plate and a PP25 measuring system was used for the characterization of photopolymerization induced shrinkage stress. To ensure good reproducibility, all measurements were conducted with 80 μl of sample formulation which was placed at the center of the glass plate. The measurements were conducted at 20 $^{\circ}\text{C}$ with a gap of 100 μm . The formulations were sheered with a strain of 1% and a frequency of 1 Hz. Polymerization was induced by UV-irradiation (500 s, 320-500 nm, 3 W cm^{-2} at the exit of the light guide) projected via a waveguide from the underside of the glass plate using an Exfo OmniCure S 2000 broadband Hg-lamp. During the measurements the normal force was recorded which correlates with the polymerization induced shrinkage stress.

DMTA

An Anton Paar MCR 301 rheometer equipped with a CTD 450 oven and a SRF 12 measurement set up was used for DMTA. The prepared polymer specimens were oscillated at a frequency of 1 Hz and a strain of 0.1%. Storage modulus and loss factor plots were recorded as a function of temperature (-100 – 200 $^{\circ}\text{C}$; heating rate 2 $^{\circ}\text{C min}^{-1}$).

Dynstat impact tests

The polymer samples (3 per formulation) for the Dynstat impact test were polished and measured according to DIN 53435 at ambient temperature. For the measurements a 0.5 J hammer was used and the final impact resistance value was normalized to the width and thickness of the tested specimen. The ratio of work necessary to break a specimen to the cross section of the sample at the fracture site yielded the desired impact resistance.

Digital light processing

The 3D structuring of the tested formulations was performed with the lithography-based additive manufacturing technology (L-AMT). A digital mirror device (DMD chip) is based between the light source, with a maximum emission of 460 nm, and the material vat. This DMD chip is used for selectively tuning individual mirrors on and off in order to selectively expose the photosensitive resin for each single layer. The light intensity on the surface of the material vat was measured to be roughly 30 mW cm^{-2} . The layer thickness was 50 μm and every layer was irradiated for 22 s. The final 3D parts were cleaned from any residual supporting material and then suspended into an isopropanol bath.

Summary of results

Table S1 Summarized results for Photo-DSC, RT-FTIR measurements, DMTA and Dynstat test.

sample	composition	t_{max} / s	$t_{95\%}$ / s	ΔH_p / kJ mol^{-1}	DBC / %	T_g / $^{\circ}\text{C}$	fwhm / $^{\circ}\text{C}$	G'_{20} / MPa	G'_r / MPa	a / kJ m^{-2}
A	UDMA/D3MA (equimolar)	4.6	65	204.6	83	150	-	987	-	2.4 ± 0.4
B	A + EAS (20 db%)	10.2	101	181.7	85-90	72	23	837	4.5	6.1 ± 1.8
C	A + EVS (20 db%)	11.8	49	226.6	91	71	23	1060	6.6	11.3 ± 1.7

References

1. D. Colombani, C. Navarro, M. Degueil-Castaing and B. Maillard, *Synth. Commun.*, 1991, **21**, 1481-1487.
2. D. H. R. Barton, C.-Y. Chern and J. C. Jaszberenyi, *Tetrahedron*, 1995, **51**, 1867-1886.