

Supporting Information for:

Exploring the benefits of β -allyl sulfones for more homogeneous dimethacrylate photopolymer networks

*Christian Gorsche,^{ab} Thomas Koch,^c Norbert Moszner,^{bd} and Robert Liska^{*ab}*

^aInstitute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163-MC, 1060 Vienna, Austria

^bChristian-Doppler-Laboratory for Photopolymers in Digital and Restorative Dentistry, Vienna University of Technology, Getreidemarkt 9/163-MC, 1060 Vienna, Austria

^cInstitute of Materials Science and Technology, Vienna University of Technology, Favoritenstrasse 9-11, 1040 Vienna, Austria

^dIvoclar Vivadent AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein

*corresponding author: robert.liska@tuwien.ac.at

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Table S1 Composition of formulations A-G.

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1. General Methods

NMR spectra were recorded on a Bruker AC 200 at 200 MHz (50 MHz for ^{13}C), and chemical shifts are given in ppm and were referenced to the solvent residual peak (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). Multiplicities are referred to as s (singlet), d (doublet), and m (multiplet). Coupling constants (J values) are given in Hz. Silica gel chromatography was performed with a Büchi MPLC-system equipped with the control unit C-620, fraction collector C-660, and UV-photometer C-635. Commercial grade reagents and solvents were used without further purification.

2. Synthesis of p-Toluenesulfonyl Iodide (pTSI)

All work steps were performed in a yellow light lab where wavelengths below 480 nm are filtered (adhesive foils of the company IFOHA were used to cover windows and fluorescent lamps). At first, iodine (9.14 g, 36 mmol) was dissolved in approximately 150 mL of ethanol and then added to a stirred solution of sodium p-toluenesulfinate (6.41 g, 36 mmol, 0.1 M in water). After the addition was completed, the reaction was stirred for another 15-30 min. Then the yellow precipitate (pTSI) was filtered by suction filtration and washed with water. Afterwards the precipitate was dissolved in a minimal amount of toluene and dried over Na_2SO_4 . The solution was then filtered into the same amount of cold petrol ether and pTSI was crystallized at -20 °C. The yellow solid was filtered, washed with cold petrol ether and dried under vacuum. pTSI was isolated in 60% yield (6.09 g). ^1H NMR (200 MHz, CDCl_3 , δ , ppm): 7.75 (d, $^3J = 8.2$ Hz, 2H; Ar-H), 7.34 (d, $^3J = 8.2$ Hz, 2H; Ar-H), 2.48 (s, 3H; Ar- CH_3); ^{13}C NMR (50 MHz, CDCl_3 , δ , ppm): 147.5 (C4), 146.3 (C4), 129.7 (C3), 125.4 (C3), 21.8 (C1). Analytical data were in accordance with literature values.¹

3. Synthesis of ((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(2-(tosylmethyl) acrylate) (DAS)

The first step of this synthesis was prepared under light protection. 2 equivalents (3.38 g, 12 mmol) of pTSI were placed into a 100 mL round bottom flask and 50 mL of CH_2Cl_2 were added. Then 1 equivalent of tetraethylene glycol dimethacrylate (1.98 g, 6 mmol) was added to the reaction solution. At this point the reaction solution was placed in the light (regular light bulb) and stirred until the methacrylate double bonds disappeared in the ^1H NMR spectra (additional TLC monitoring). The reaction took approximately 3 h. After the completion of the reaction step, 50 mL of ethyl acetate was added to the reaction solution and all following steps were again performed under light protection. CH_2Cl_2 was evaporated and the ethyl acetate phase washed with a 5 wt% solution of sodium dithionite (2 x 30 mL) and water (2 x 30 mL). The collected aqueous phase was reextracted with 30 mL of ethyl acetate and the combined organic phase was dried over Na_2SO_4 . The solution was filtered and placed into a three-neck round bottom flask with a reflux condenser. The reaction was flushed with argon and 5 equivalents of freshly distilled triethylamine (3.04 g, 30 mmol) were slowly added. The reaction was refluxed and the progress of the reaction was tracked via ^1H NMR analysis. After completion of the reaction, the solution was cooled and then washed with 1 N HCl (2 x 50 mL) and water (50 mL). The aqueous phase was reextracted with ethyl acetate and the combined organic phase dried over Na_2SO_4 . The solvent was evaporated and the crude

product was purified via silica column chromatography (PE/EtOAc: 1/3). DAS was isolated in 70% yield (2.68 g).

^1H NMR (200 MHz, CDCl_3 , δ , ppm): 7.73 (d, $^3J = 8.2$ Hz, 4H; Ar-H), 7.32 (d, $^3J = 8.2$ Hz, 4H; Ar-H), 6.52 (s, 2H; $=\text{CH}_2$), 5.89 (s, 2H; $=\text{CH}_2$), 4.14 (m, 8H; OOC-CH_2- , SO_2-CH_2-), 3.62 (m, 12H; $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$), 2.43 (s, 6H; Ar- CH_3); ^{13}C NMR (50 MHz, CDCl_3 , δ , ppm): 164.9 (C=O), 144.9 (C4), 135.4 (C4), 133.6 (C2), 129.7 (C3), 128.9 (C4), 128.8 (C3), 70.7 (C2), 68.8 (C2), 64.5 (C2), 57.5 (C2), 21.6 (C1); Anal. calcd. for $\text{C}_{30}\text{H}_{38}\text{O}_{11}\text{S}_2$: C 56.41, H 6.00, S 10.04; found: C 56.36, H 5.89, S 9.84.

Table S1 Composition of formulations A-G.

Formulation	Composition
A	UDMA/D3MA 1/1 (mol%)
B	A/DAS (16.67 mol%)
C	A/DAS (20 mol%)
D	A/DAS (25 mol%)
E	A/DT (16.67 mol%)
F	A/DT (20 mol%)
G	A/DT (25 mol%)

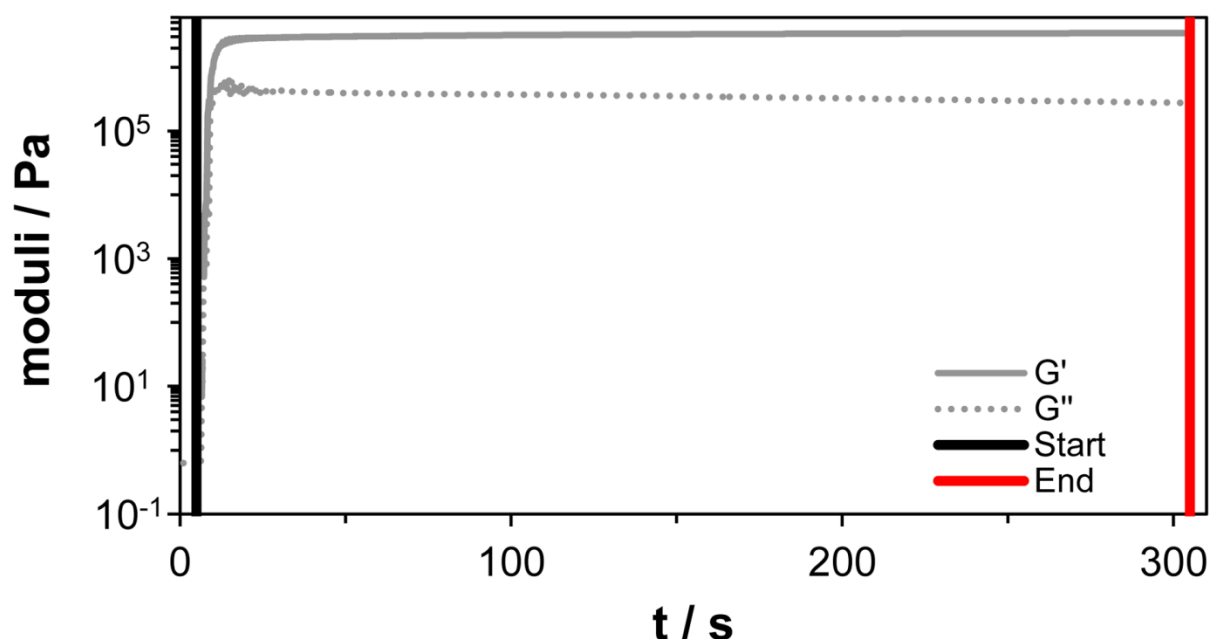


Fig. S1 Photorheology plots of formulation A (start of light at 5s, black line; end of light at 305 s, red line).

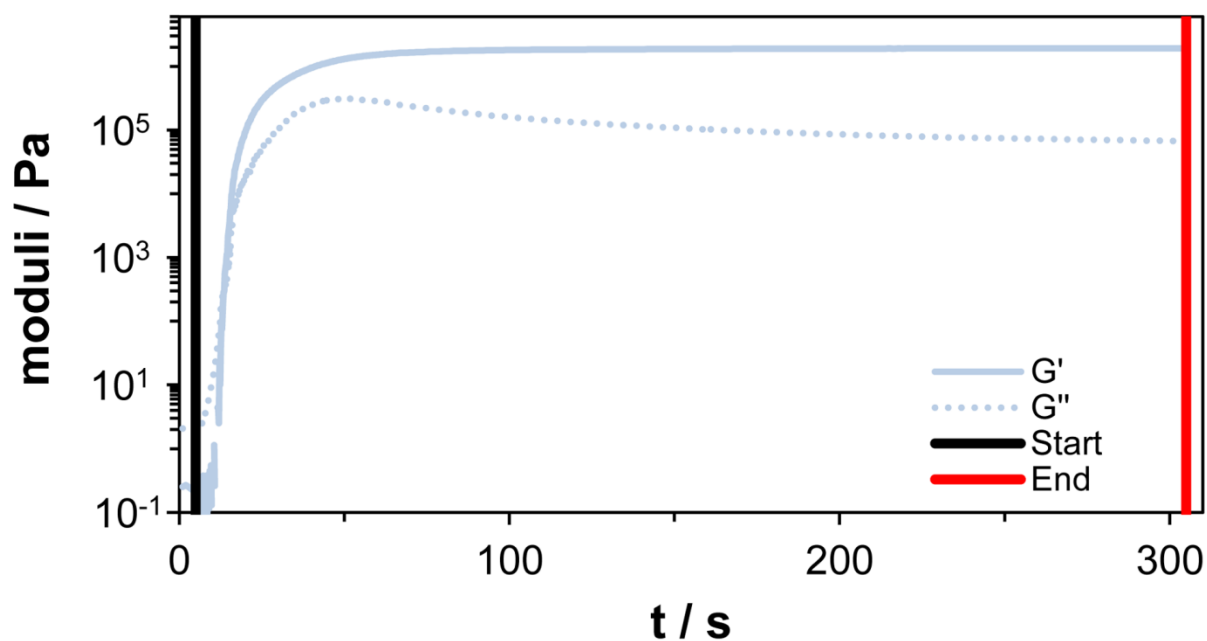


Fig. S2 Photoreology plots of formulation B (start of light at 5s, black line; end of light at 305 s, red line).

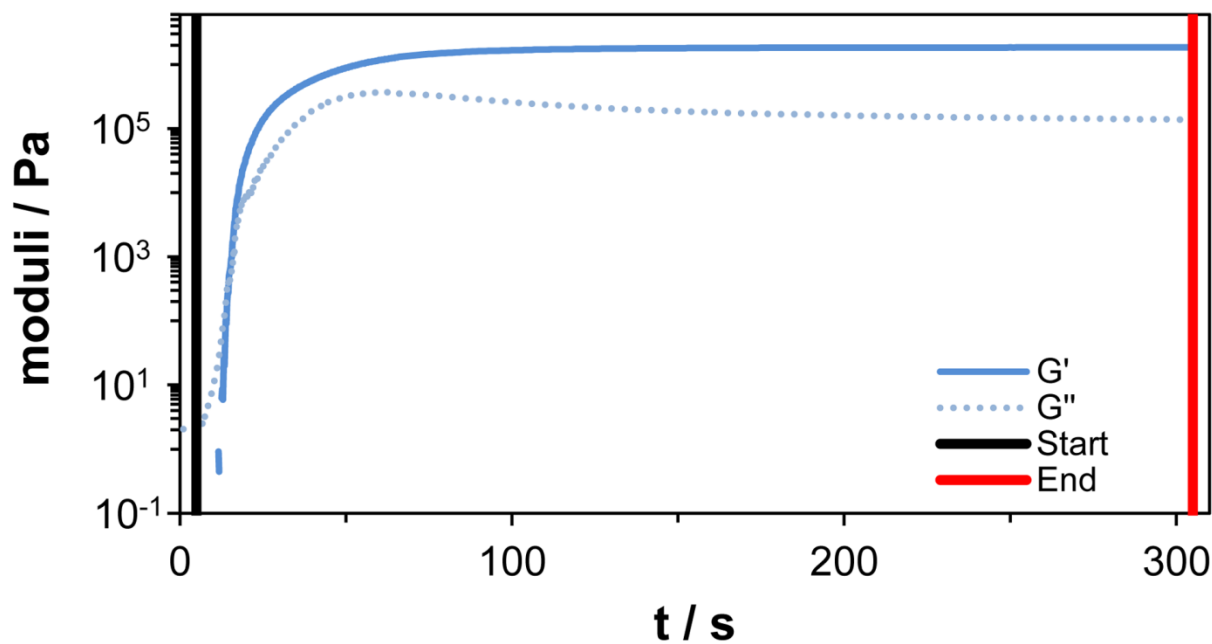


Fig. S3 Photoreology plots of formulation C (start of light at 5s, black line; end of light at 305 s, red line).

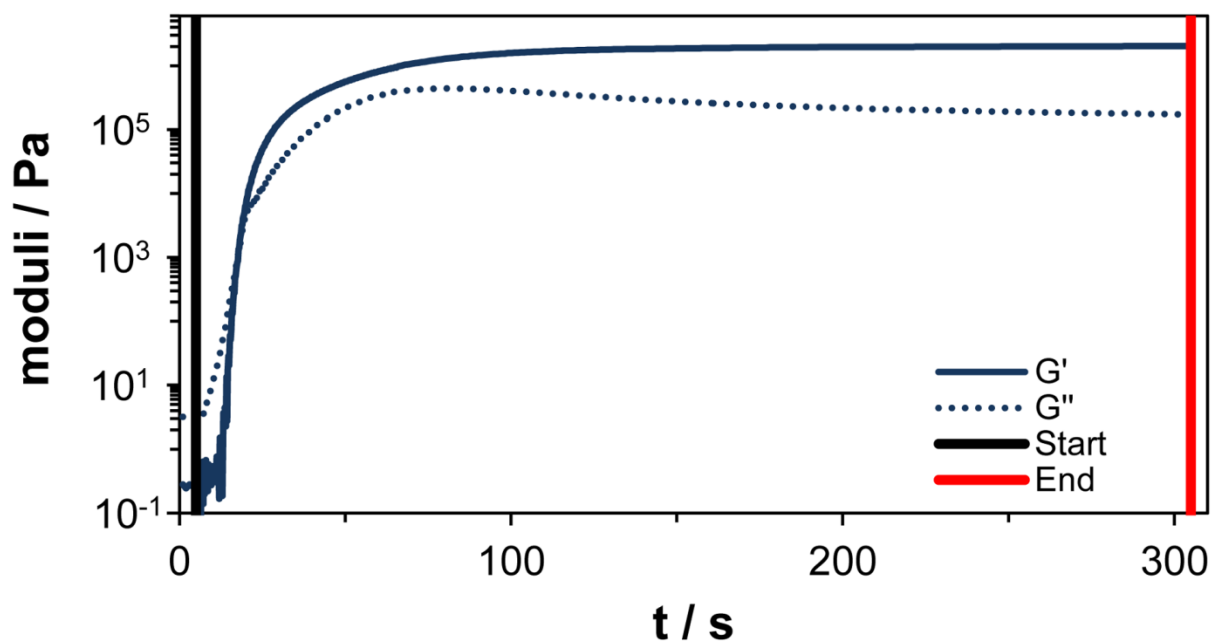


Fig. S4 Photorheology plots of formulation D (start of light at 5s, black line; end of light at 305 s, red line).

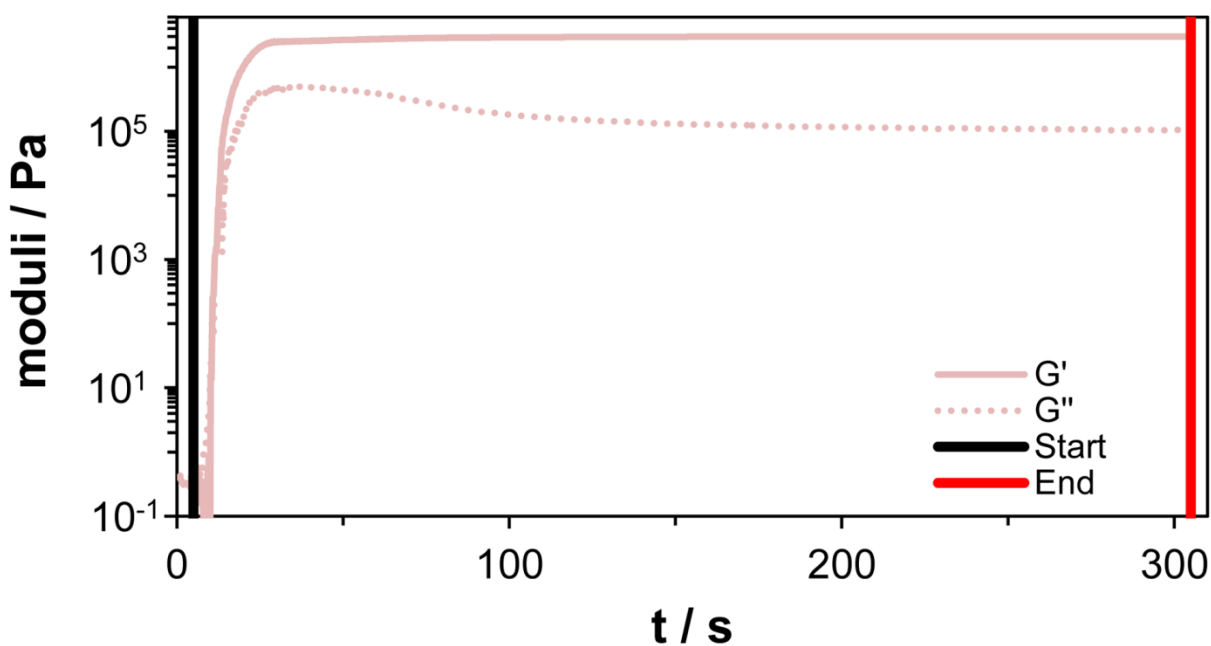


Fig. S5 Photorheology plots of formulation E (start of light at 5s, black line; end of light at 305 s, red line).

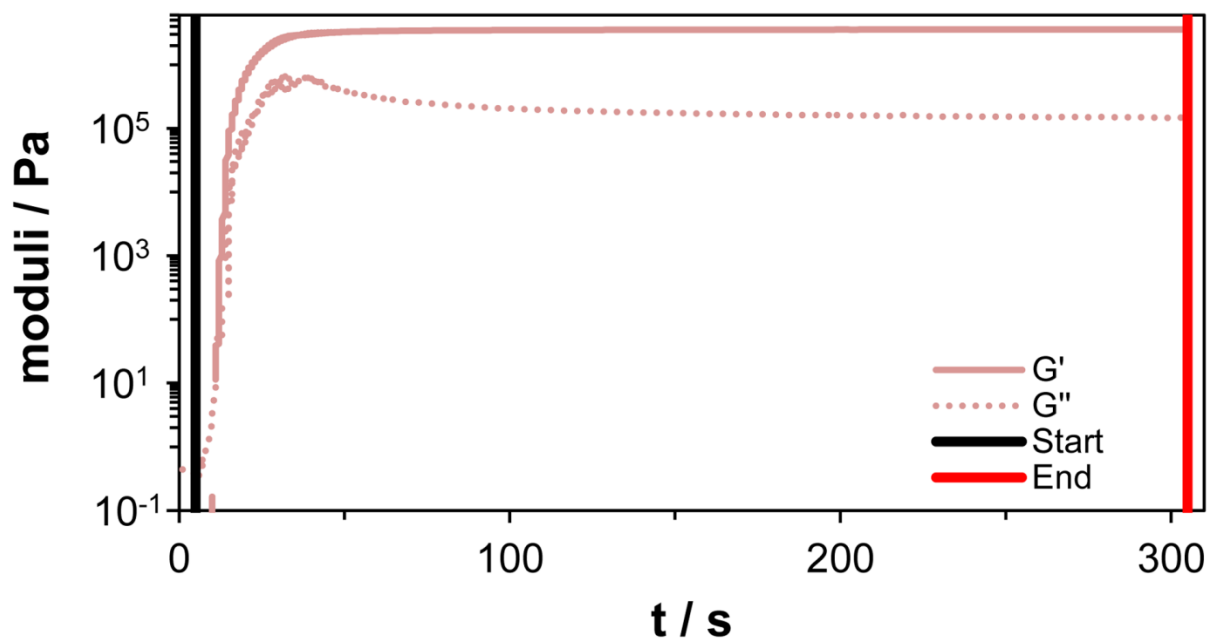


Fig. S6 Photoreology plots of formulation F (start of light at 5s, black line; end of light at 305 s, red line).

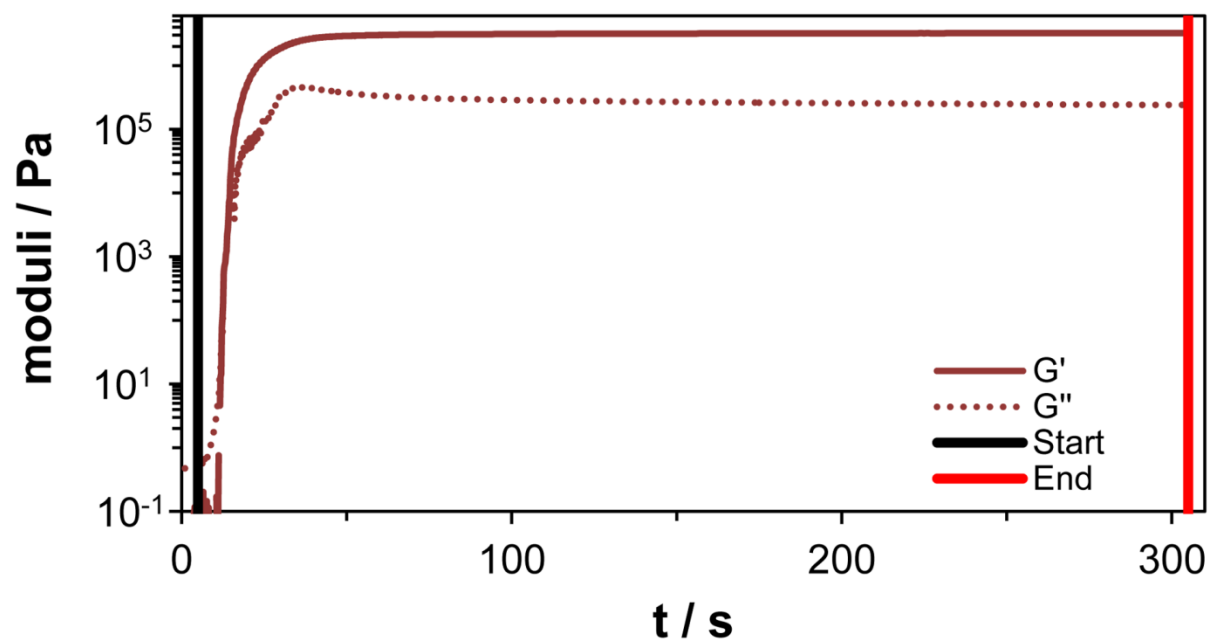


Fig. S7 Photoreology plots of formulation G (start of light at 5s, black line; end of light at 305 s, red line).

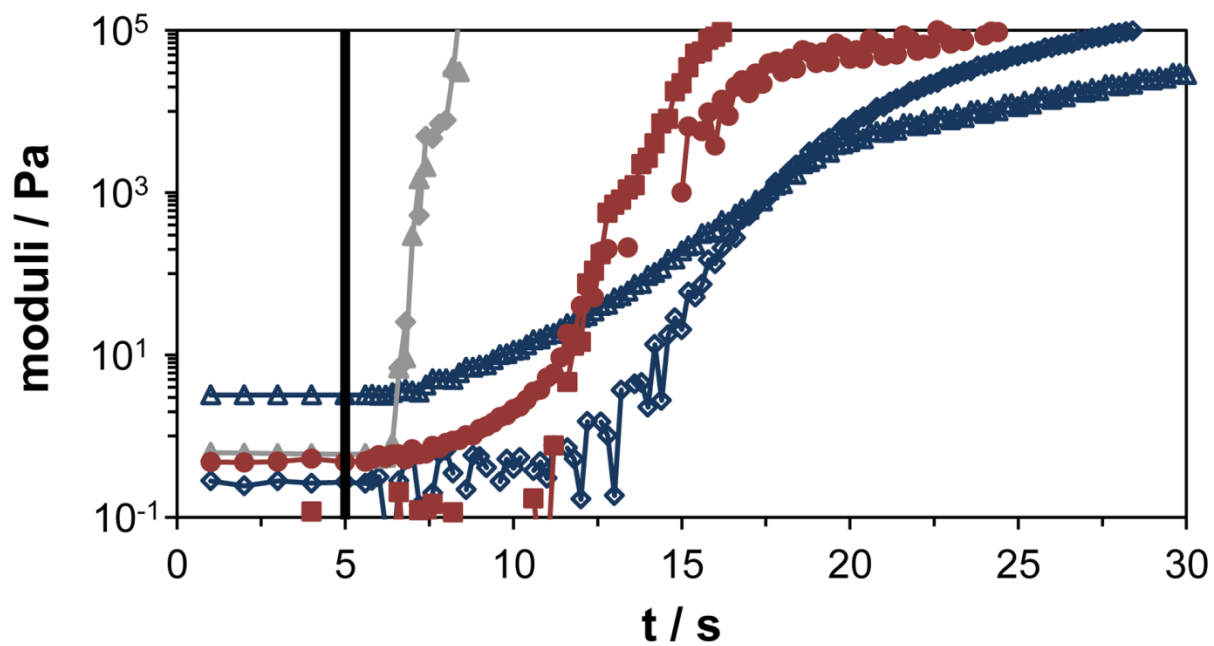


Fig. S8 G' (A \blacklozenge , D (DAS25) \diamond , and G (DT25) \blacksquare) and G'' (A \blacktriangle , D \triangle , and G \bullet) plots during photocuring.

REFERENCES

1. G. L. Edwards, C. A. Muldoon and D. J. Sinclair, *Tetrahedron*, 1996, **52**, 7779-7788.