

Supporting Information

Spatially resolved photoactivation of dynamic exchange reactions in 3D-printed thiol-ene vitrimers

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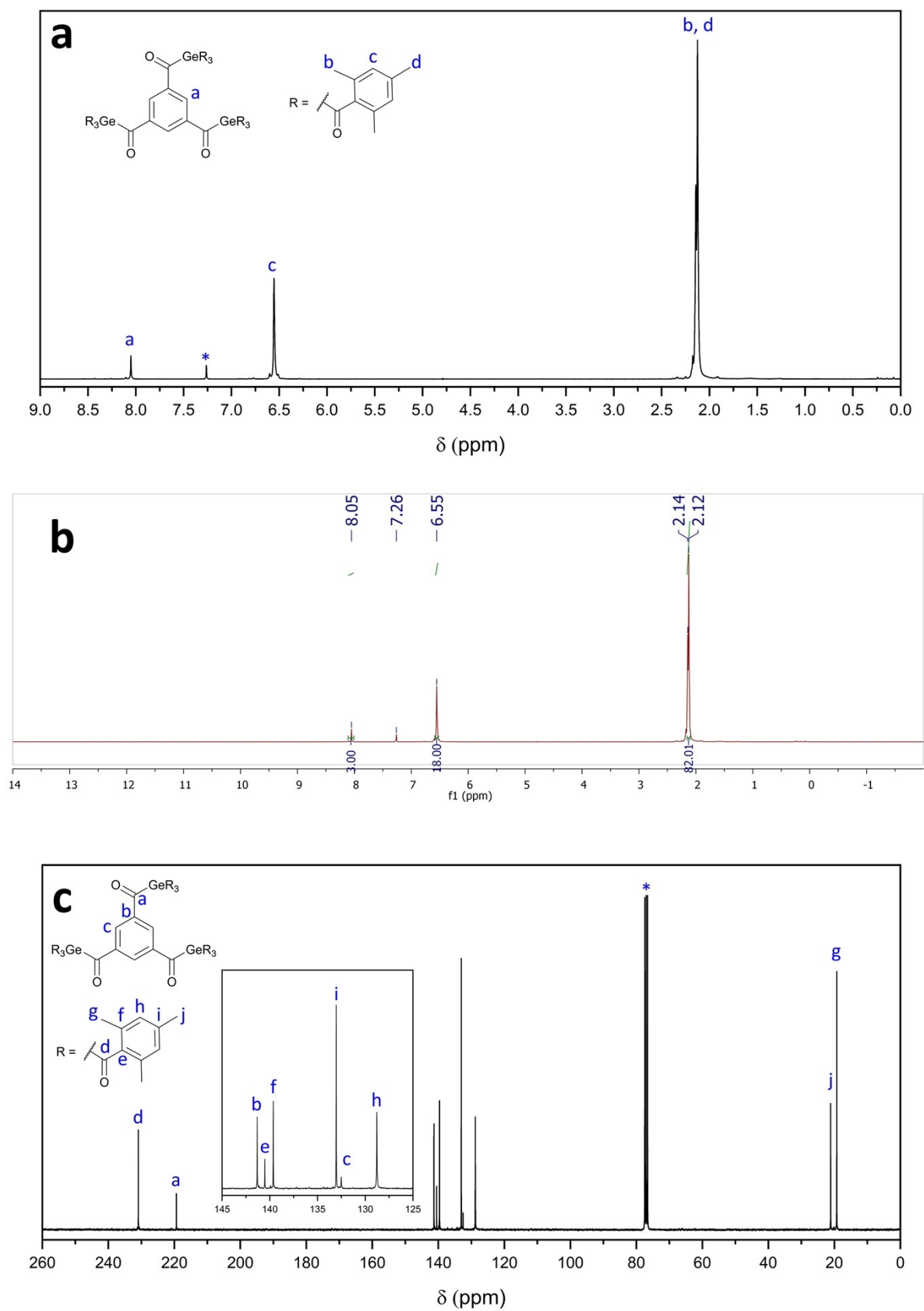


Fig. S1 ^1H NMR (300 MHz, CDCl_3) peak specification (a) and integration (b) of Ge-PI. ^{13}C NMR (75 MHz, CDCl_3) peak specification of Ge-PI. (*) indicates the solvent peak.

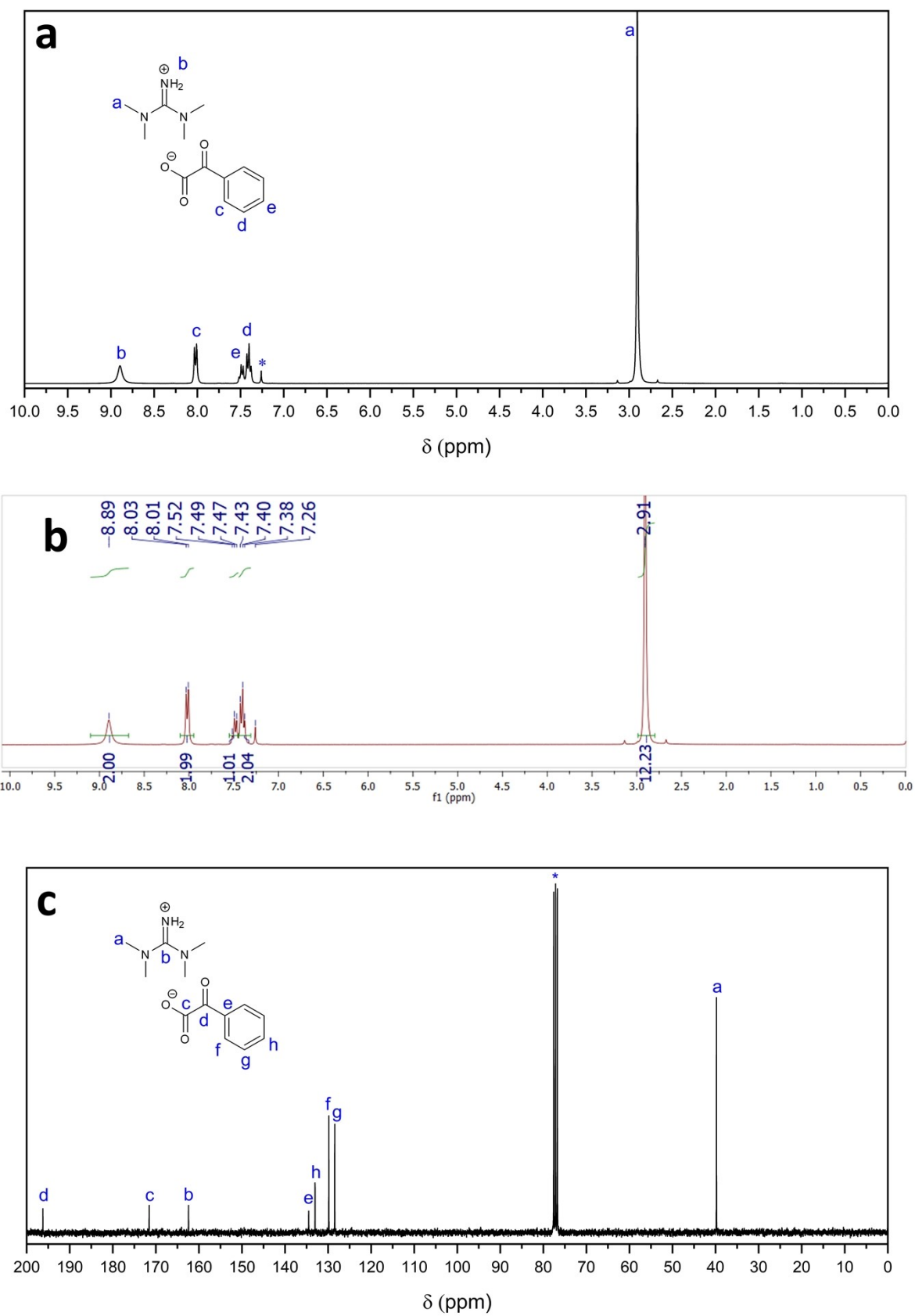


Fig. S2 ¹H NMR (300 MHz, CDCl₃) peak specification (a) and integration (b) of TMG-PLB. ¹³C NMR (75 MHz, CDCl₃) peak specification of TMG-PLB. (*) indicates the solvent peak.

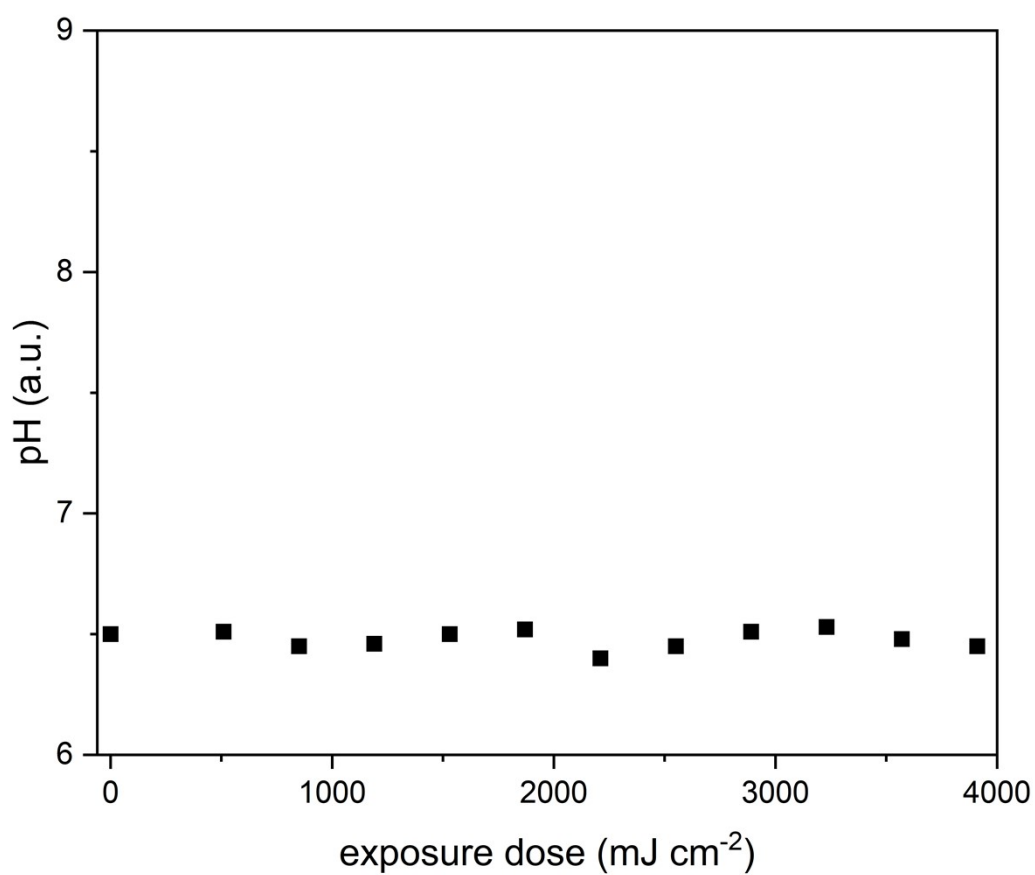


Fig. S3 pH measurements in an aqueous solution of TMG-PLB (0.06 mol L^{-1}) upon irradiation with 450 nm LED light (17 mW cm^{-2}).

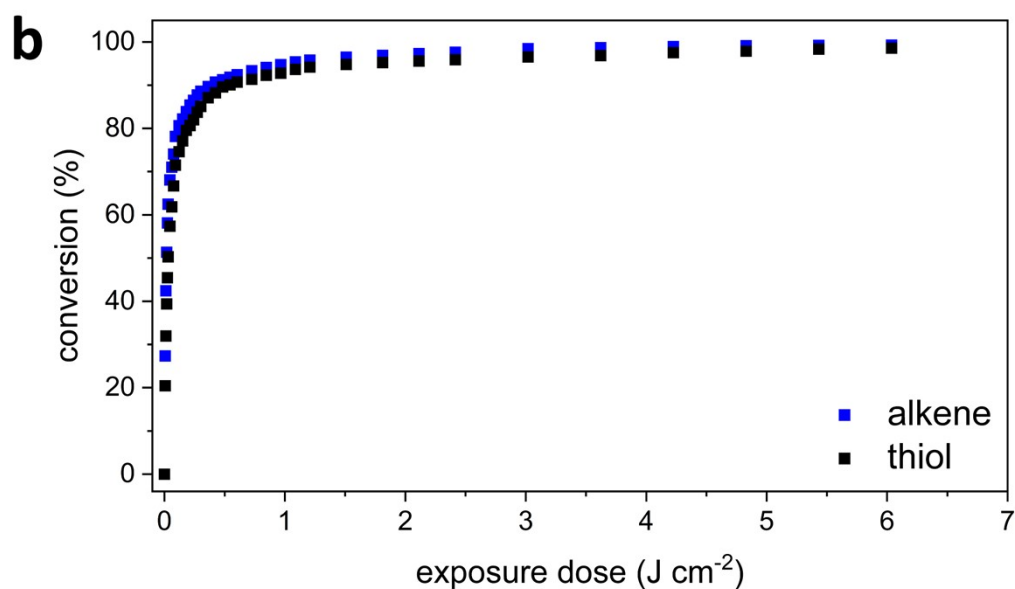
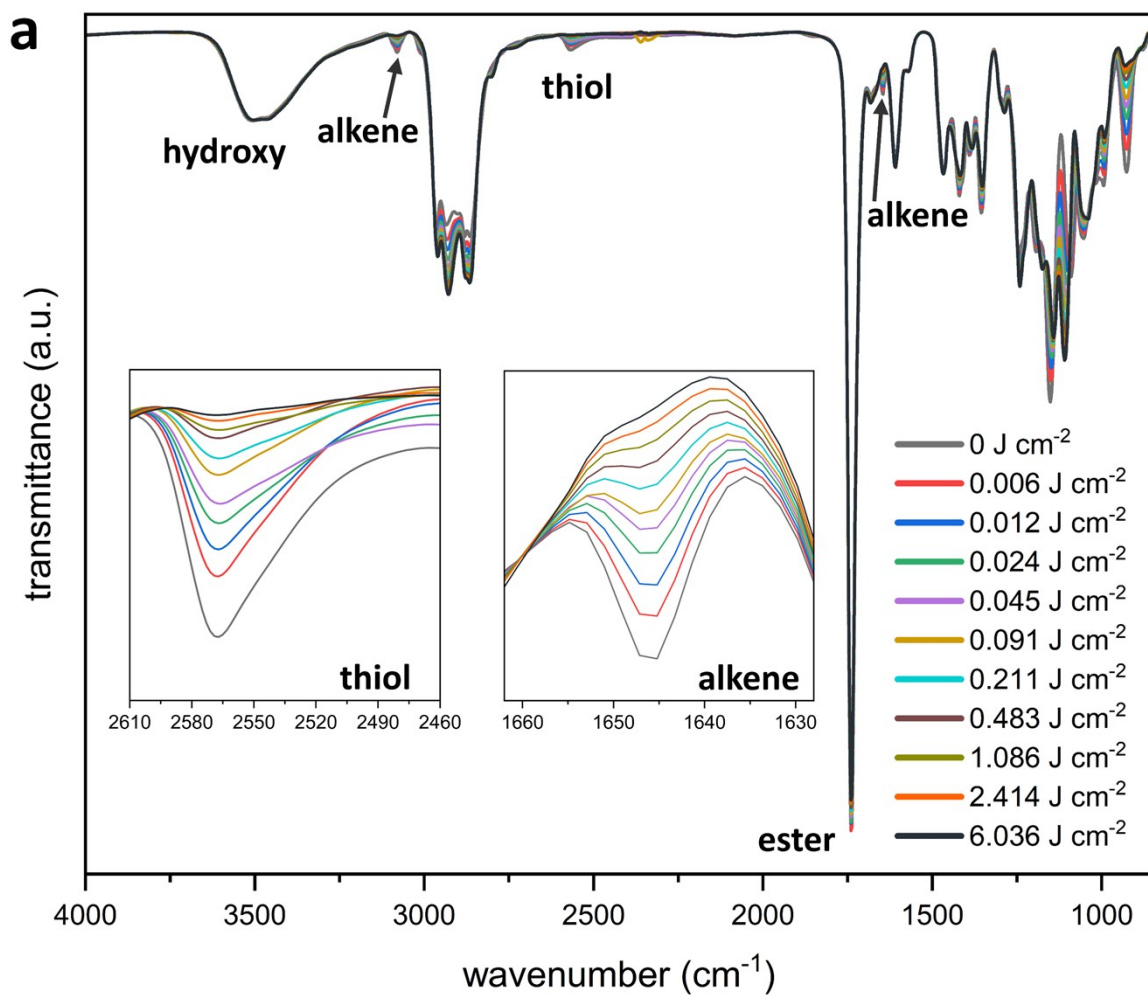


Fig. S4 Curing kinetics of the thiol-ene resin formulation examined by FTIR spectroscopy in transmission mode upon irradiation with 450 nm LED light. (a) FTIR absorption spectra at different exposure doses. Insets magnify the regions of alkene (C=C) and thiol (S-H) stretching vibrations. (b) Alkene (double bond) and thiol conversion monitored through the decrease of the corresponding absorption bands at 1645 and 2569 cm⁻¹, respectively.

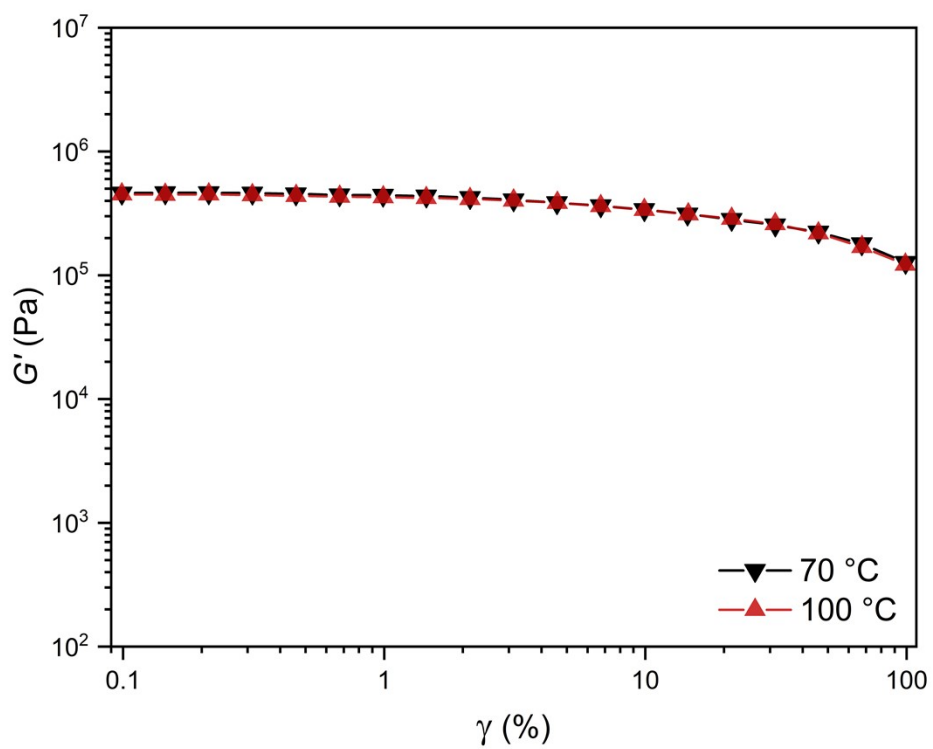


Fig. S5 Amplitude sweep measurements acquired from unactivated specimens at 70 and 100 °C with an oscillation frequency of 1 Hz. The storage modulus (G') is plotted versus the applied deformation (γ).

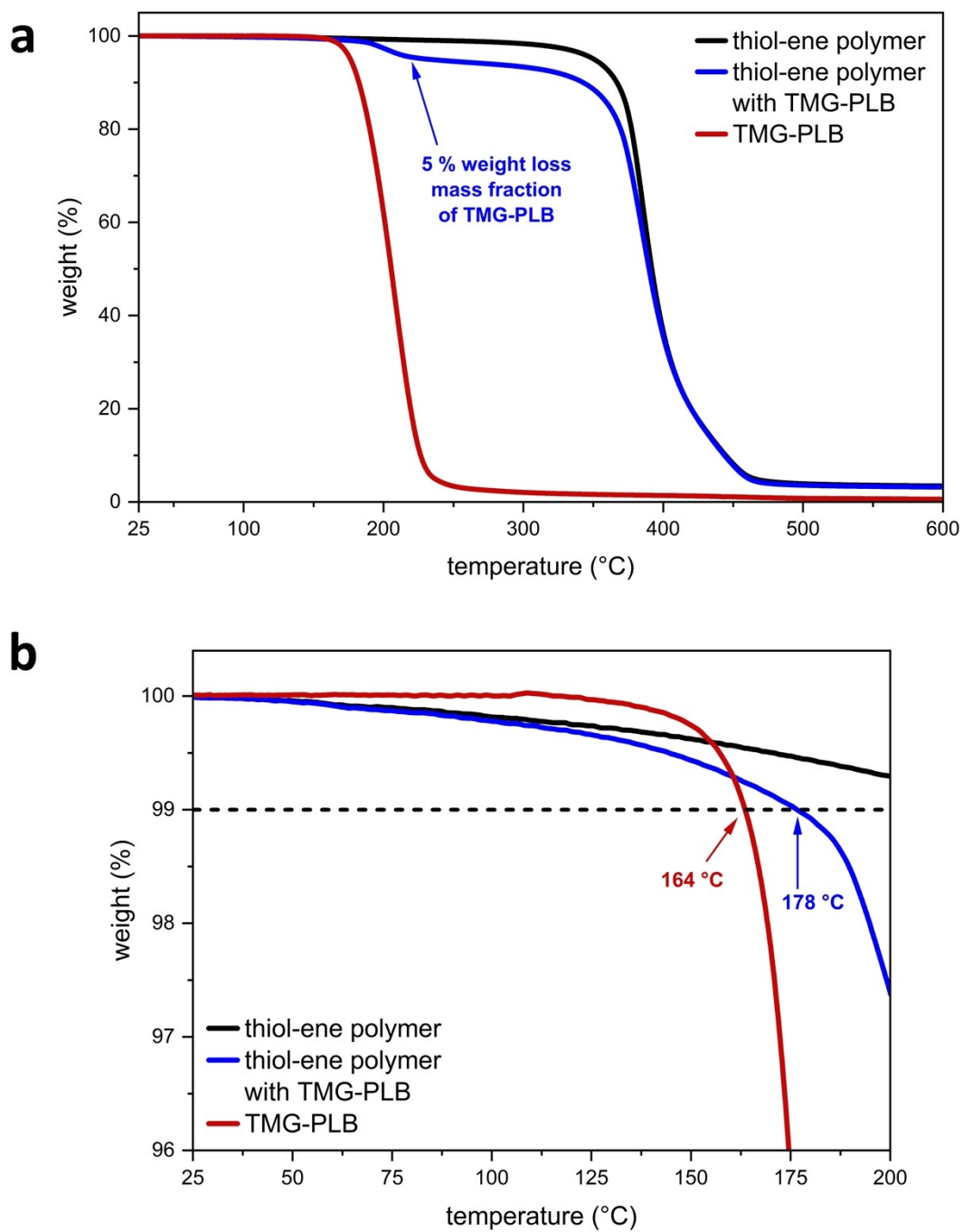


Fig. S6 (a) TGA of the thiol-ene polymer (without incorporated TMG-PLB), the (unactivated) thiol-ene polymer with incorporated TMG-PLB and pure TMG-PLB. All measurements were carried out under nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. (b) Magnification of the initial mass losses in the temperature region of 25 to 200 °C.

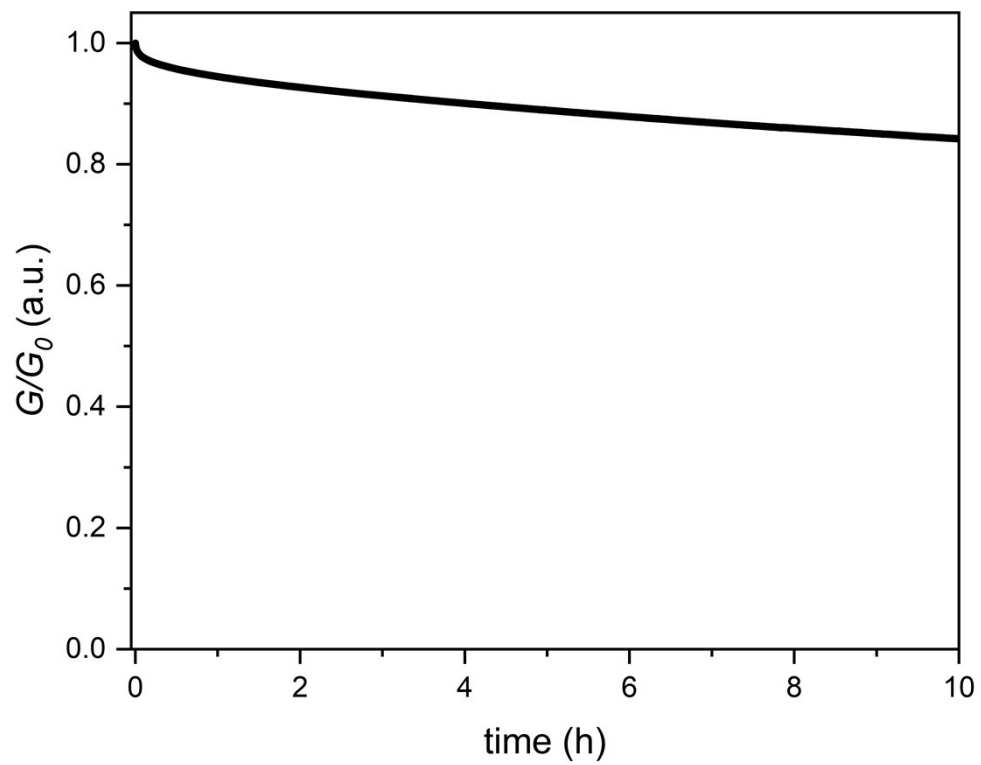


Fig. S7 Stress relaxation behaviour on a photoactivated (580 J cm^{-2} 405 nm LED light) sample at room temperature.

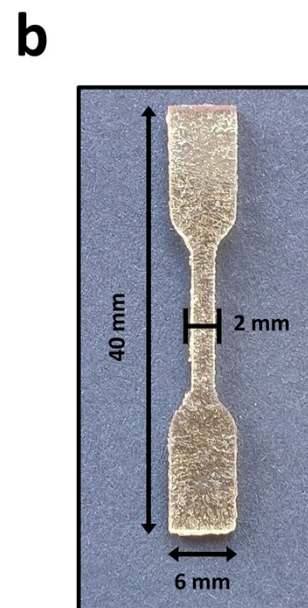
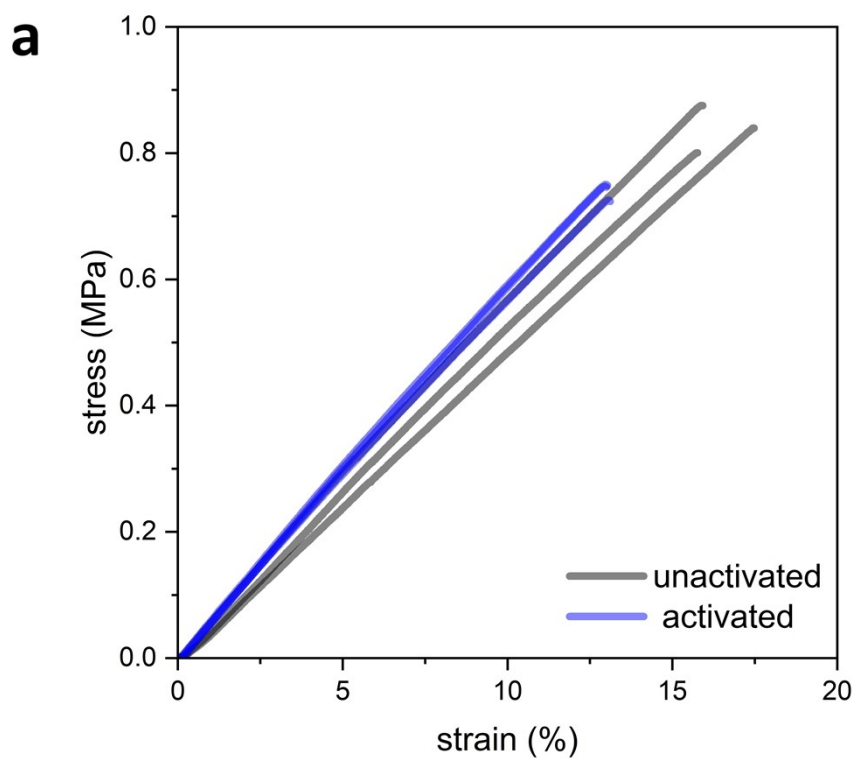


Fig. S8 (a) Stress strain curves obtained at crosshead speed of 5 mm min^{-1} from unactivated and prior to the measurement photoactivated (580 J cm^{-2} 405 nm LED light) samples. (b) Example of a 1.5 mm thick dumbbell test specimen with dimensions.

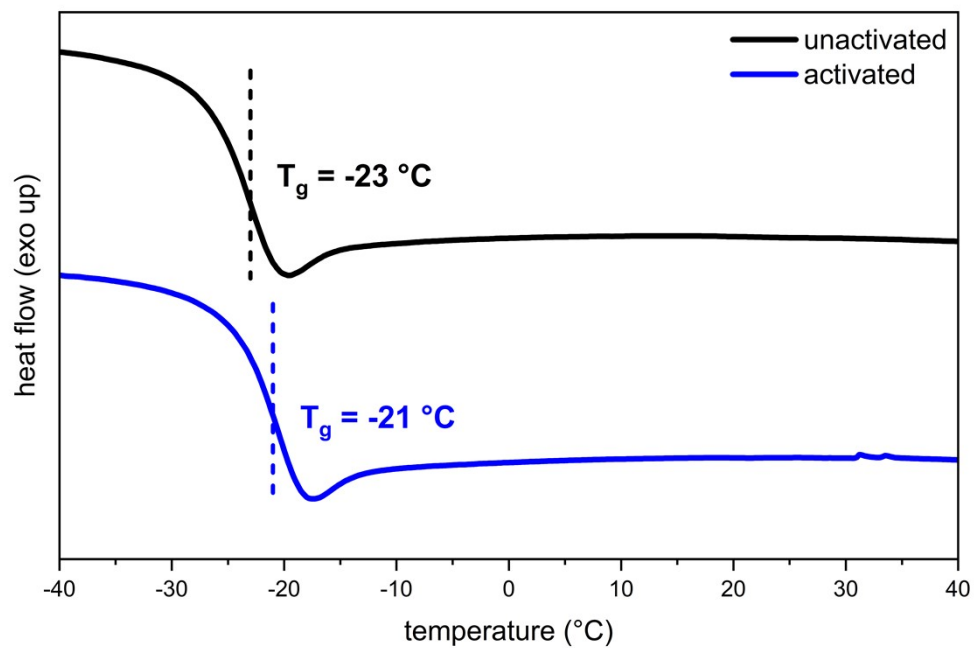


Fig. S9 DSC measurements performed with an unactivated and an prior to the measurement activated (580 J cm^{-2} 405 nm LED light) sample at a heating rate of 10 °C min^{-1} .

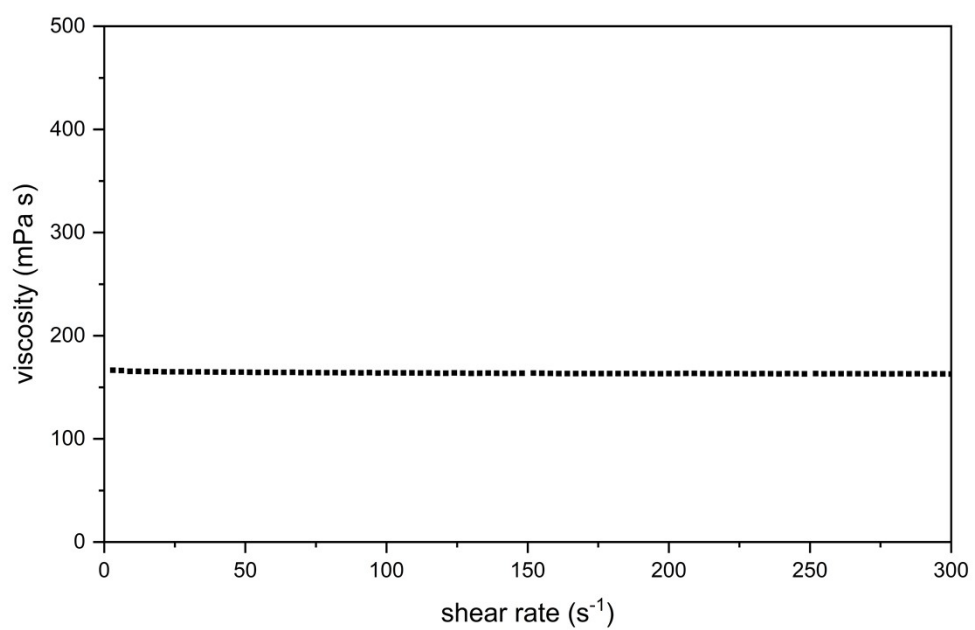


Fig. S10 Viscosity of the thiol-ene resin formulation determined at 25 °C with a shear rate linearly increased from 3 to 300 s⁻¹.

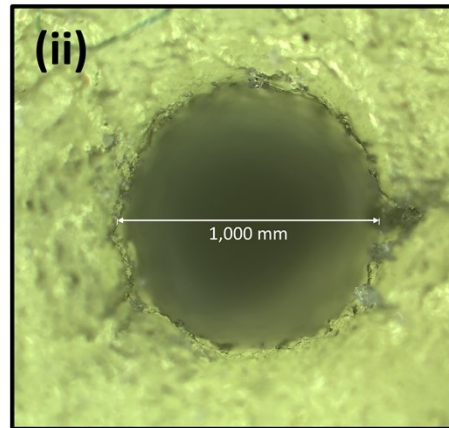
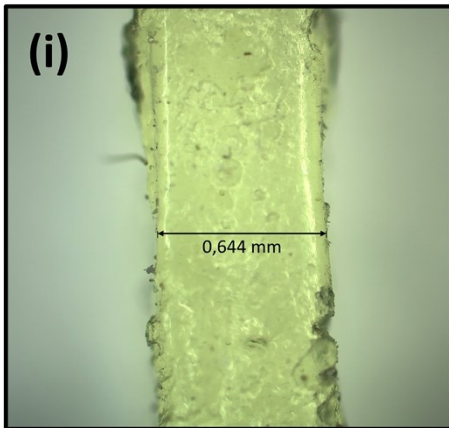
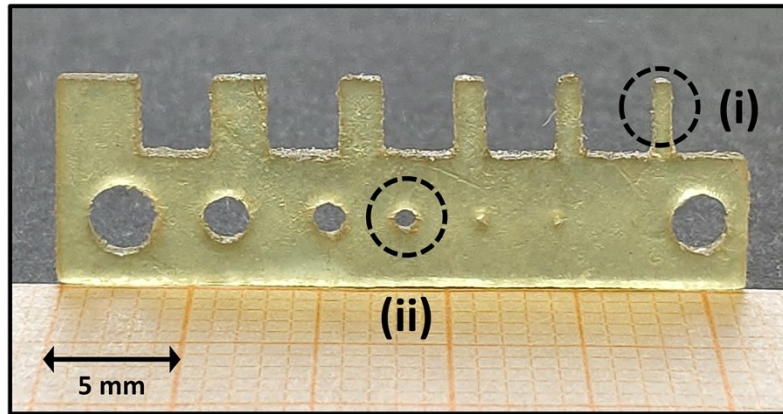


Fig. S11 Photograph and microscope images of a DLP 3D-printed comb-like object for illustrating the achievable printing resolution. The structure was printed along the flattest axis (final layer facing to the front).

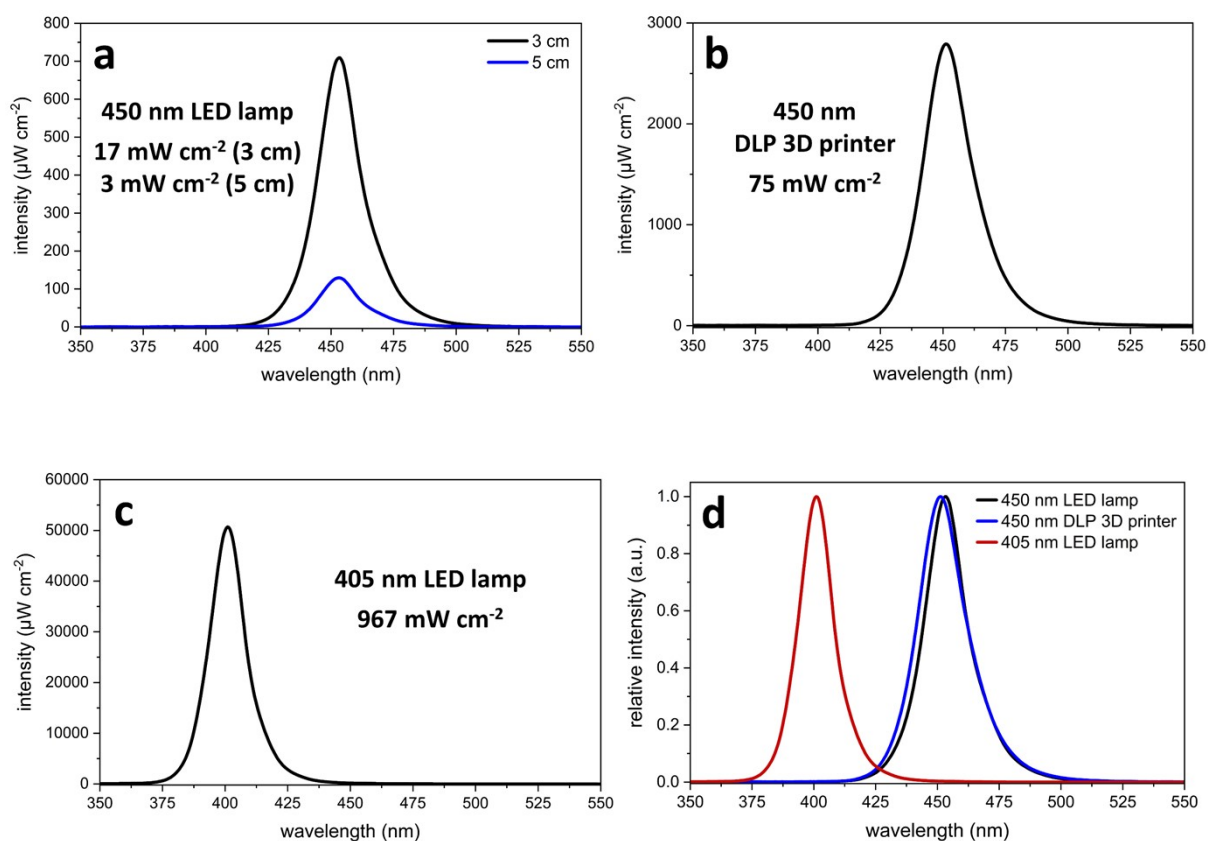


Fig. S12 Emission spectra with corresponding intensity values of all irradiation sources used: (a) 450 nm LED lamp in the distance of 3 and 5 cm, (b) 450 nm DLP 3D printer at the settings used for object manufacturing and (c) 405 nm LED lamp in the distance of 4 cm. (d) Normalized representation of the emission spectra.