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Laser-triggered writing and biofunctionalization of thiol-ene networks

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FT-IR and Polymerization Kinetics

For sample preparation, few drops of resin formulation were placed on a silicon wafer and cast with a film applicator bar of 12 μm . The cast film was irradiated using a Hamamatsu LC8 lamp with visible bulb and a cut-off filter below 400 nm with an intensity of 8 mW/cm^2 ($\lambda > 400 \text{ nm}$) in order to cure the mixture.

FT-IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Milano, IT) in transmission mode in the wavenumber range between 450 and 4000 cm^{-1} . The absorption peak areas were calculated with OMNIC software. The kinetics of the light-induced thiol-ene reaction were monitored by the depletion of the IR absorption signals representing the thiol groups (2569 cm^{-1}) and the carbon double bonds (1640 cm^{-1}). The conversion was further estimated as follows:

$$\text{conversion} = (1 - (A_0/A_t)) * 100.$$

where, A_0 and A_t correspond to the peak area of the IR absorption band prior to and after a selected time of light exposure.

The network formation occurs upon the radical-mediated thiol-ene click reaction between the double bonds of vinyl-NBE and thiol groups of TMPMP (Fig S1). Upon visible light exposure, the photo-initiator (BAPO) undergoes α -bond cleavage mechanism (Norrish type I system) in which free radicals are formed. Those radicals abstract a hydrogen from thiol moieties yielding thiyl radicals (RS^*) (Figure S1).^[1]

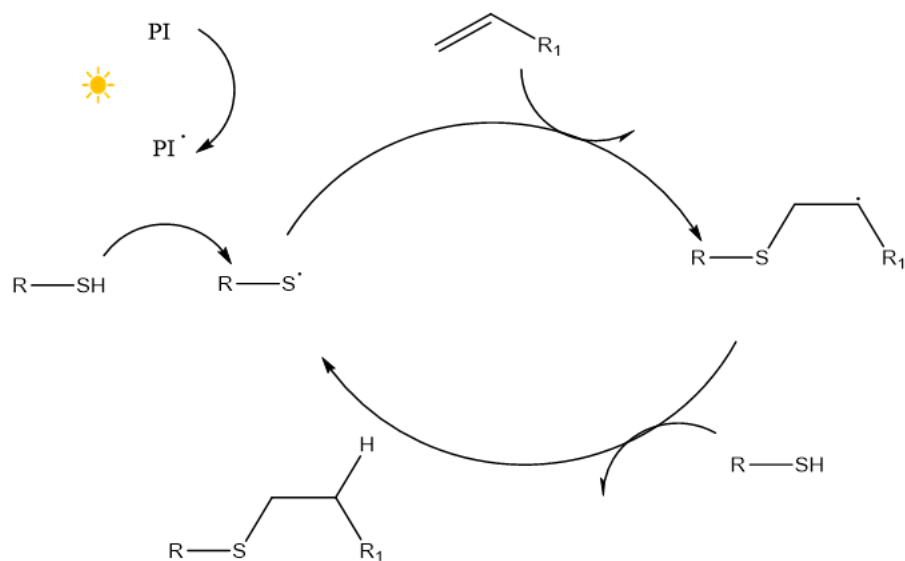


Figure S1: Radical mediated mechanism of the thiol-ene reaction.^[1,2]

Once formed, the thiyl radicals initiate the polymerization within two steps: first the direct addition of the thiyl radical across the C=C bond, yielding an intermediate carbon-centered radical followed by chain transfer to a second molecule of thiol to give the thiol-ene addition product, with the concomitant generation of a new thiyl radical. Possible termination reactions involve typical radical-radical coupling processes.^[2]

Regarding the kinetics of the thiol-ene reaction, the molecular properties of both thiol and vinyl monomers influence the reaction rate. At a given thiol moieties, the reaction rate is affected by the structure of carbon-carbon double bonds and particularly by the electron density nearby the double bond functionalities. Within few exceptions, the reaction rate increases with rising electron density.^[1,2] The lower electron density of the vinyl NBE may explain the lower reactivity rate compared to other thiol-ene formulations. Moreover -NO₂ moieties could also interact with radicals, reducing the speed of the reaction.

IR spectra of the thiol-ene system were collected at different irradiation times: in Figure S2a we report the comparison between the liquid and the cured formulation while the kinetics is shown in Figure S2b. The kinetics of the vinyl-NBE/TMPMP system in Figure S2b shows a fast conversion rate of both thiol and C=C groups in the first 60 seconds of irradiation, reaching a final plateau after 300 seconds at about 88 % of conversion. These kinetics are in agreement with a previous work on thiol vinyl-NBE systems.^[2] The C=C and SH conversions shown in Figure S2b proceed with a similar reaction rate and final conversion, indicating that co-polymerization is occurring. The high final conversion in this system (88%), compared to other radical mediated

reactions such as methacrylic, is a typical key feature of the thiol-ene based system, in which the delay in gel point allows chain mobility inside the network until higher conversions.^[1,2]

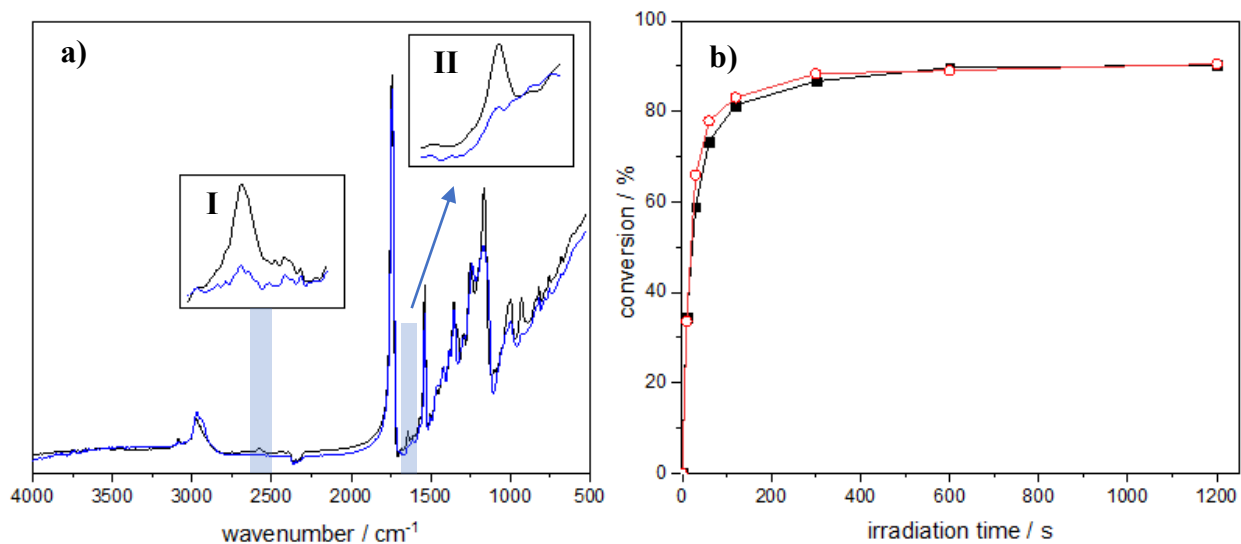


Figure S2: a) FT-IR spectra of TMPMP/vinyl-NBE formulation prior (black) to and after (blue) photo-curing (3.6 J/cm^2 , $\lambda > 400 \text{ nm}$, air). Inserts show the IR bands of the characteristic (I) SH (2569 cm^{-1}) and (II) C=C (1640 cm^{-1}) groups magnified out of the FT-IR spectra. b) Normalized depletion of the thiol absorption band (2580 cm^{-1}) solid square and double carbon bonds absorption band (1640 cm^{-1}) (open circles) versus illumination time (8 mW/cm^2 , $\lambda > 400 \text{ nm}$, air).

Thermo-mechanical characterization

In order to characterize the thermomechanical properties of the cured polymer networks, dynamic-mechanical analysis (DMA) and differential scanning calorimetry (DSC) were carried out.

The samples used in DMA and DSC measurements were prepared placing the formulations inside a rectangular mold of $20 \times 15 \times 0.4 \text{ mm}$ and curing it with a Hamamatsu LC8 lamp with

visible bulb and a cut-off filter below 400 nm with an intensity of 4 mW/cm² ($\lambda > 400$ nm) for 20 minutes.

DMA measurements were carried out using a Triton Technology TTDMA in the range between -90 and 50 °C at a frequency of 1 Hz and displacement of 20 μ m; DSC measurements were performed with a METTLER DSC-30 (Greifensee, Switzerland) instrument, equipped with a low temperature probe. The samples were heated up in nitrogen atmosphere twice from -90 to 150 °C with a heating rate of 10 K/min, the second scan was analyzed.

The cured films were then characterized by DMA and DSC. The T_g in DMA measurement is calculated as the temperature corresponding to the maximum of $\tan \delta$ curve and it is approximately -10 °C. This is in good agreement with DSC measurements ($T_g = -13$ °C).

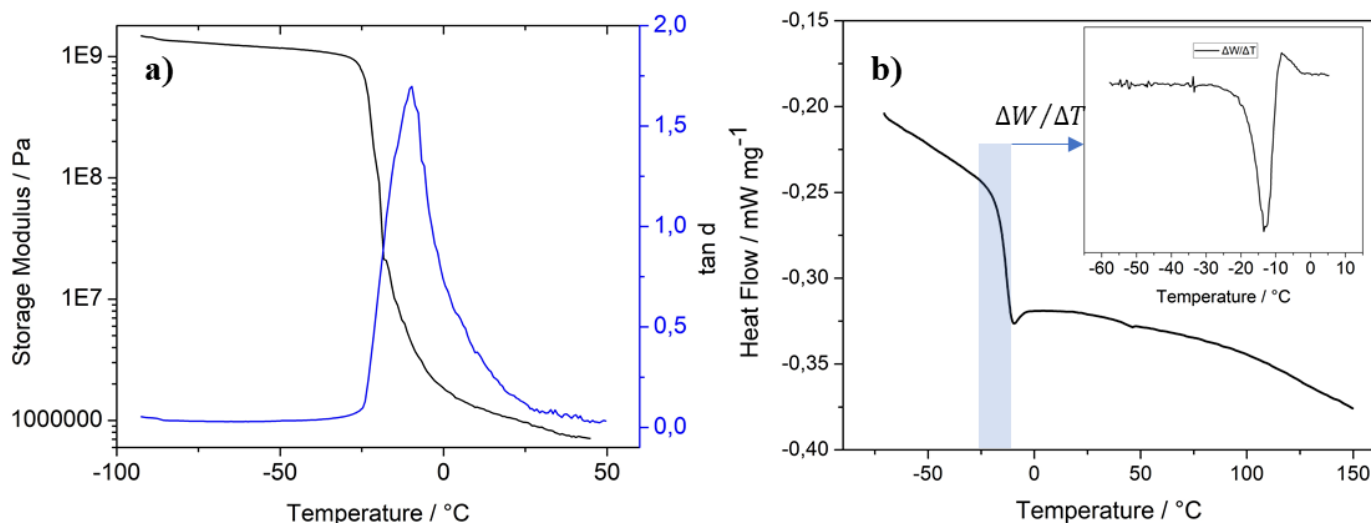


Figure S3: a) DMA measurement of TMPMP/vinyl-NBE sample with storage modulus (black) and $\tan \delta$ (blue) of the crosslinked polymer b) heat flow/temperature curve according to DSC measurement of the TMPMP/vinyl-NBE formulation with insert (I) of first derivate of the heat flow; $\Delta W/\Delta T$ in the glass transition interval.

Degradation Mechanism of *o*-NBE

The photo-cleavage of the *o*-NBE links occurs by illuminating the cured samples with UV-light (between 320-380 nm). The reaction proceeds *via* biradical intermediates formed by β -hydrogen abstraction by the excited nitro group analogous to the Norrish-type II reaction (see Figure S4).^[3-5] In the triplet state, a proton abstraction from the methylene or methine carbon in γ -position takes place by an oxygen atom from the nitro group, which is followed by the generation of an *aci*-nitro tautomer in the ground state. The latter can undergo cyclization to form a benzisoxazole derivative. The resonance stabilized five-membered ring is subsequently cleaved yielding a carboxylic acid and an *o*-nitrosobenzaldehyde as primary photoproducts. In secondary photoreactions the formed *o*-nitrosobenzaldehyde dimerizes and is able to form azobenzene groups (see Figure S4b).^[3-5]

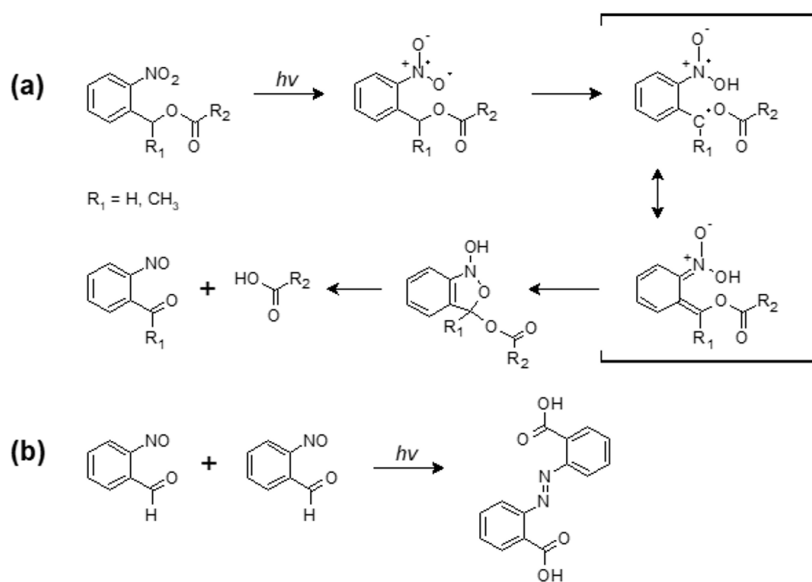


Figure S4: (a) Primary and (b) secondary photoreactions during the photoisomerization of *o*-NBE derivatives.^[3-5]

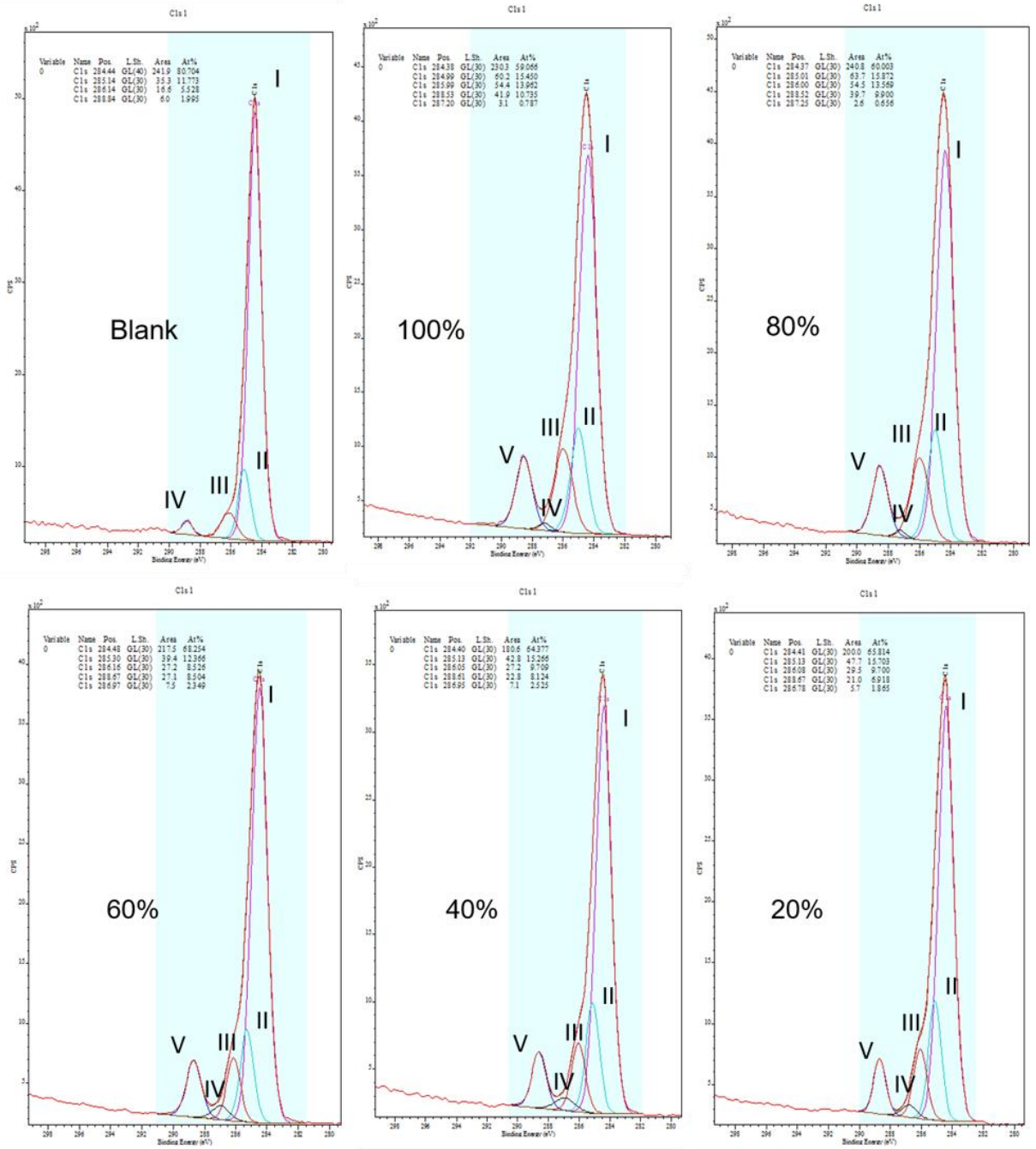


Figure S5: High Resolution C1s XPS peaks for the blank sample and the samples irradiated with different laser energy doses.

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