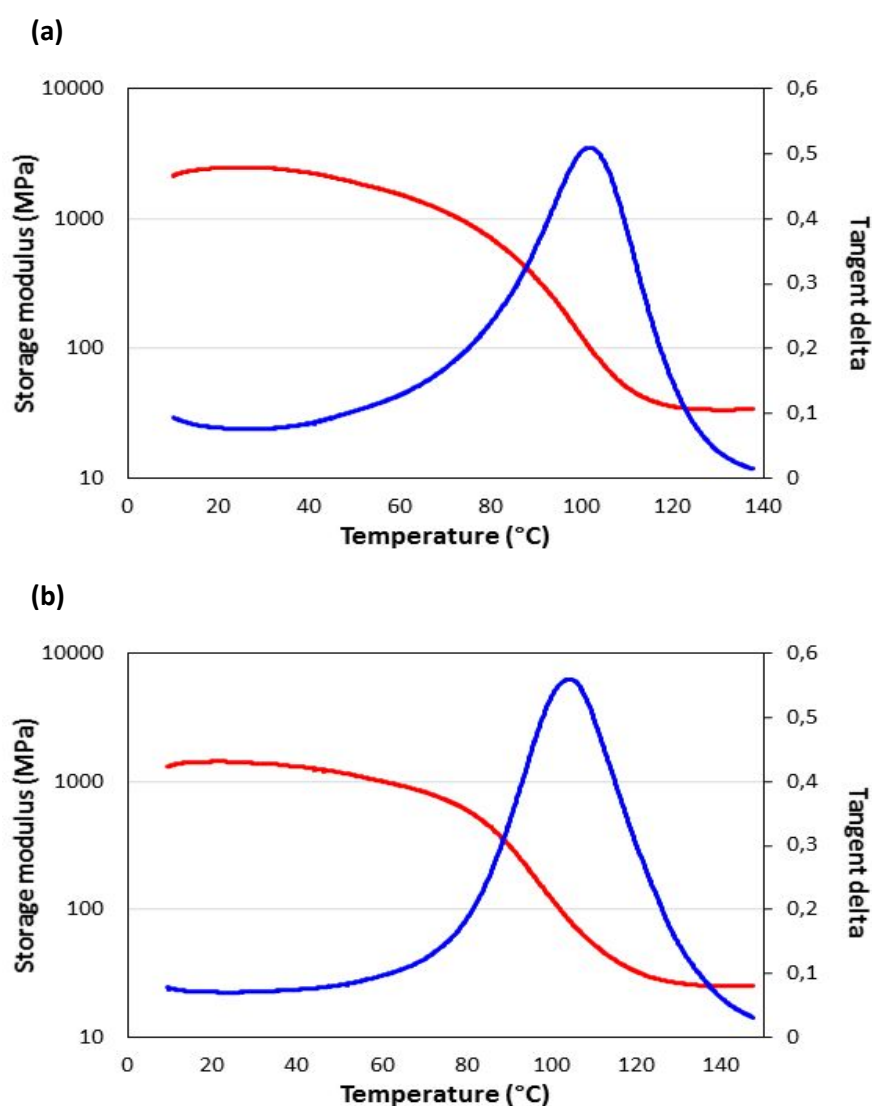


**Thermal metamorphosis in (meth)acrylate photopolymers: stress relaxation, reshaping, second-stage curing**

*Maciej Podgórski<sup>1,2</sup>, Brady Worrell<sup>1</sup>, Jasmine Sinha<sup>1</sup>, Matthew McBride<sup>1</sup>, Christopher N. Bowman<sup>1\*</sup>*

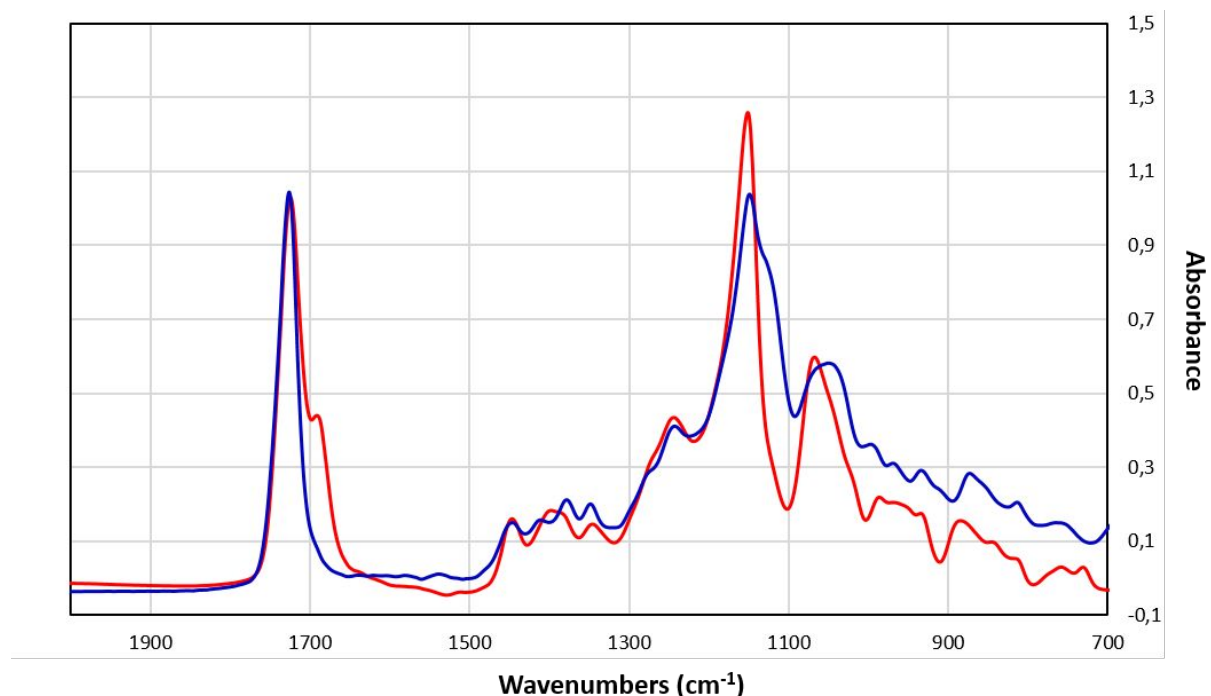
<sup>1</sup>Department of Chemical and Biological Engineering, University of Colorado, UCB 596, Boulder, Colorado 80309, United States

<sup>2</sup>Department of Polymer Chemistry, Faculty of Chemistry, Maria Curia-Skłodowska University, pl. Marii Curie-Skłodowskiej 5, 20-031 Lublin, Poland

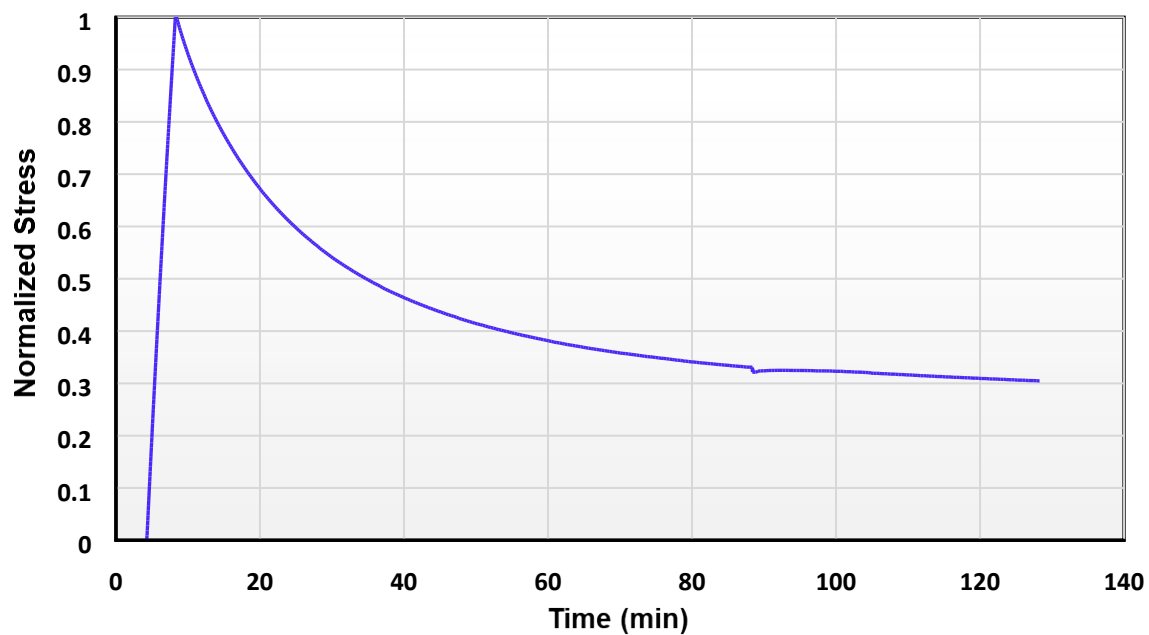


**Fig. S1.** Dynamic mechanical analysis (DMA) of dynamic methacrylate thioester material (a) composed of DMTE (dimethacrylate thioester monomer), HEMA (2-hydroxy ethyl methacrylate) and DMAP (N,N-

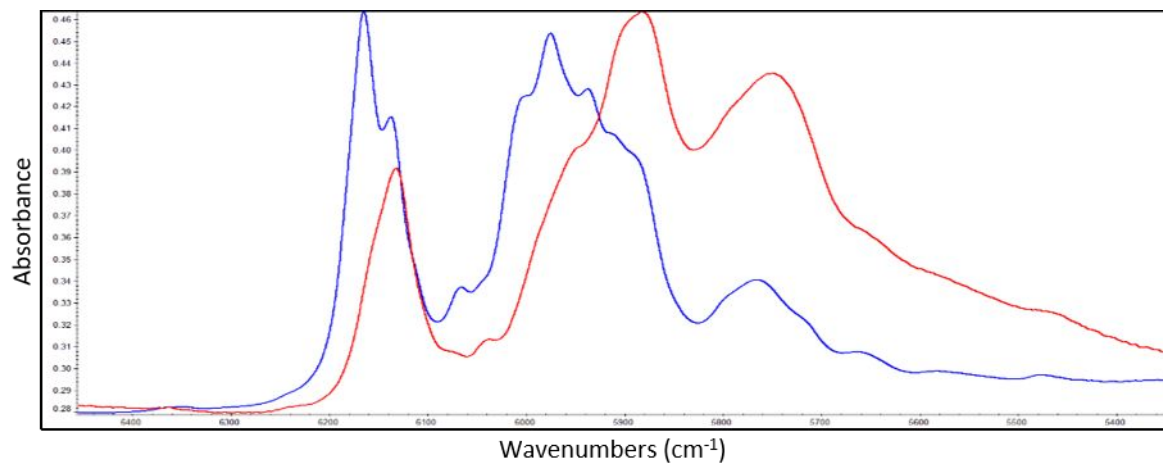
dimethylamino pyridine), and nondynamic thioester equivalent (b) composed of DMTE, HEMA and HMA (hexyl methacrylate – acting as plasticizer).



**Fig. S2.** Mid-IR spectra of a mixture of diacrylate thioester (1M) and 2-hydroxyethyl acrylate (2M) before (red) and after catalyst inclusion (blue). As exchange catalyst TMG was used in 5 mol% in respect to the thioester. Second IR was collected 10 min after TMG was added and mixed at ambient temperature. Complete consumption of the thioester carbonyl peak is apparent. Concomitantly, the first-stage UV-initiated polymerization of such resins resulted in soft gels due to the undesired thiol-acrylate addition reaction, diacrylate cleavage, and consumption of double bonds.

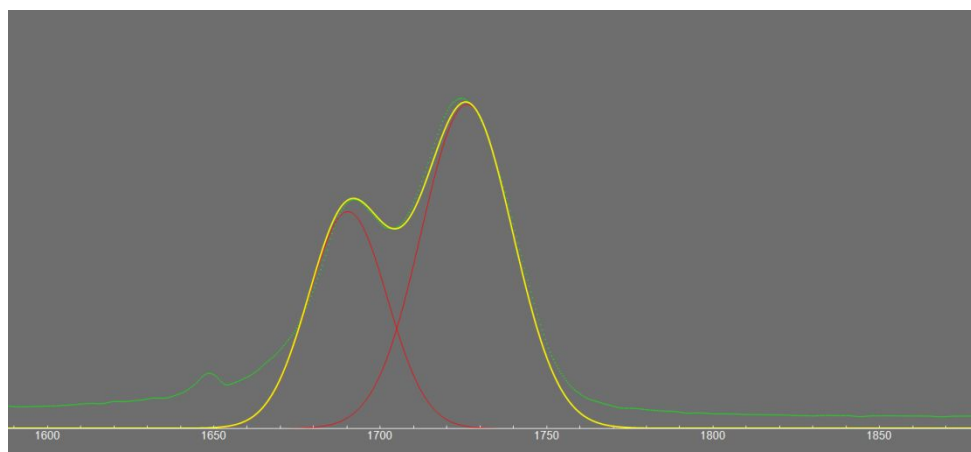


**Fig. S3.** DMA stress relaxation profile in inter-chain thioester methacrylate dynamic network. Experiment conditions: strain 5 %, strain rate 1%/min, temperature 105 °C, relaxation time 2h.

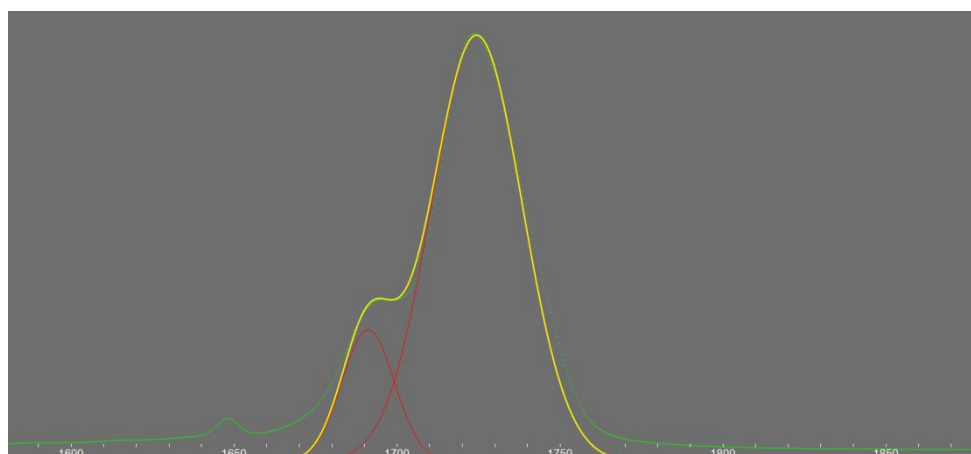


**Fig S4.** Near-IR of AA before (blue) and after (red) homopolymerization. Deconvolution brings acrylate conversion of around 90%, and allyl conversion of 30-40%.

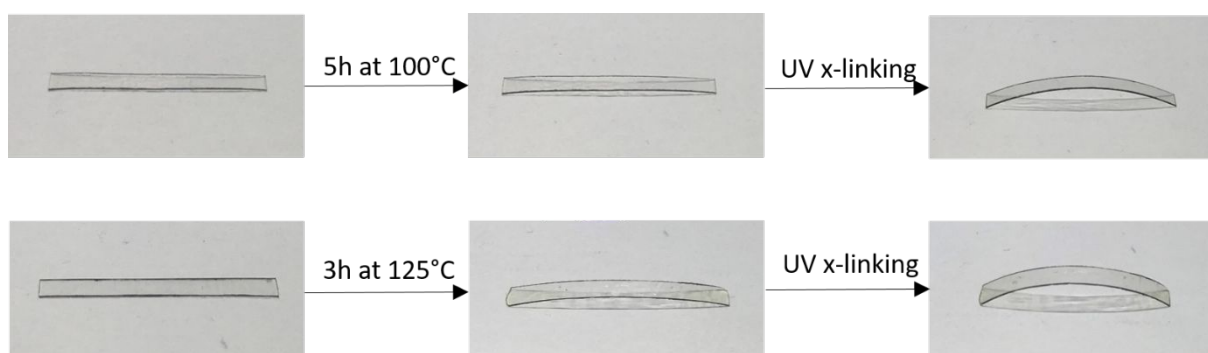
(a)



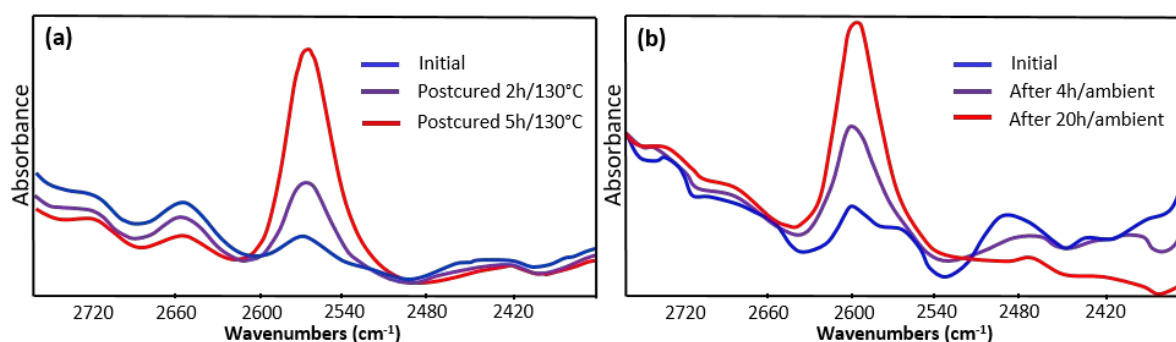
(b)



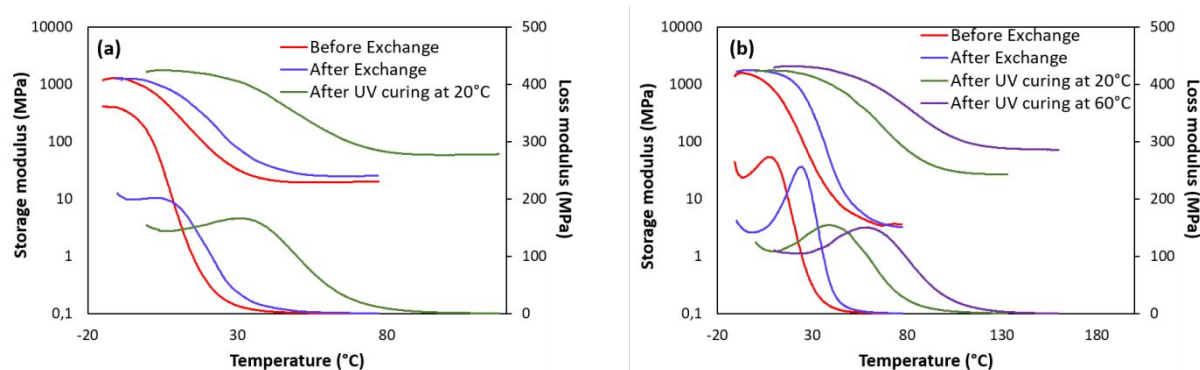
**Fig. S5.** Thioester carbonyl peak deconvolution for acrylate dynamic networks containing hydroxyls at a distance from thioesters: (a) initially cured sample prior to side-chain exchange; (b) thermally annealed sample after thermally induced metamorphosis for 5 h at 130 °C. The original ATR-IR spectra are depicted in green. Simulated profiles are in red and yellow, respectively.



**Fig. S6.** Metamorphosis and second-stage UV reshaping experiments for acrylate thioester/hydroxyethyl acrylate system: TEPA/HEA/AA/TMPTA (1.5M/1M/1M/0.1M). The samples ( $l = 20$  mm) were deformed around a cylinder ( $d = 8$  mm), and heated for 3-5 h at 100-125 °C. Afterwards, the samples were deformed again and exposed to UV irradiation.



**Fig. S7.** FTIR comparison of non-catalytic (a) and catalytic (b) side-chain metamorphosis in methacrylate systems where pendant thioesters are in close vicinity to hydroxyls. Non-catalytic side-chain thermal metamorphosis results in 55-60% conversions of hydroxyls with concomitant thiol generation. Catalytic side-chain metamorphosis results in ambient exchange leading to around 65 % hydroxyl and thioester conversions.



**Fig. S8.** Storage and loss moduli results for (a) acrylate and (b) methacrylate two-stage photopolymers with the ability for side chain metamorphosis. Included is data on sample before exchange, after thermal processing, and after second stage curing.