SPATIAL CONTROL OF DYNAMIC THIOESTER-NETWORKS USING PHOTOBASE GENERATORS

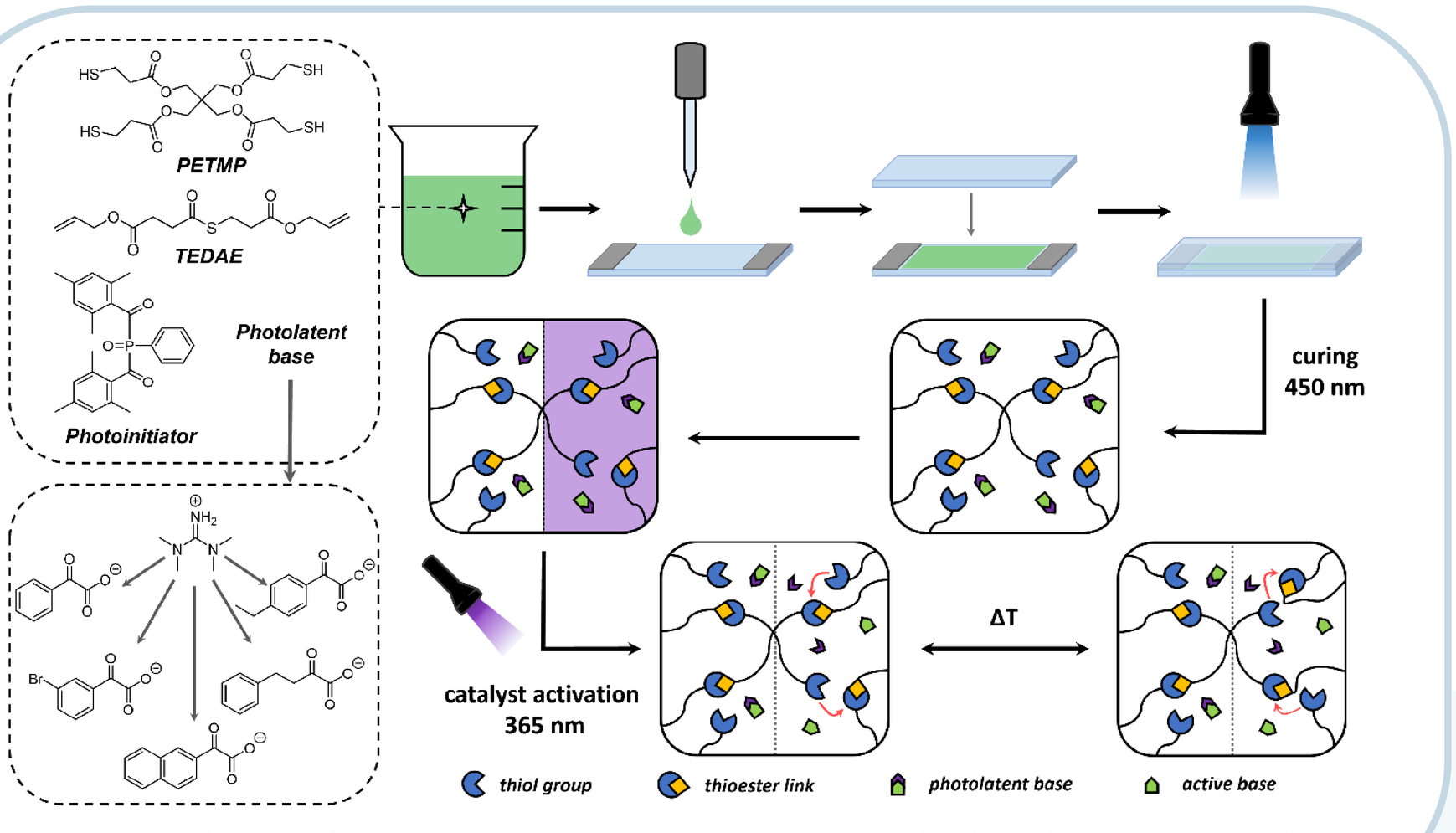
P.-M. Egger[1,2], S. Schlögl[1], G. Trimmel[2] and E. Rossegger[1]

[1] Polymer Competence Center Leoben GmbH (PCCL), Roseggerstraße 12, 8700 Leoben, Austria – pia-maria.egger@pccl.at
[2] Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

Polymer Competence Center Leoben

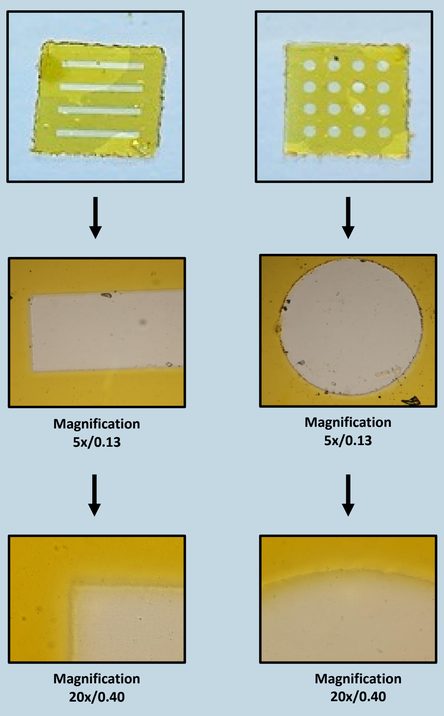
COVALENT ADAPTABLE NETWORKS

Covalent adaptable networks (CANs) combine the mechanical robustness and chemical stability of thermosets with the processability and recyclability of thermoplastics. These networks are composed of covalently crosslinked polymer chains with exchangeable bonds that enable a rearrangement of their topology in response to an external stimulus. Especially, CANs containing thioester groups are interesting for biomedical application, due to their rapid exchange mechanism, which can be initiated even at low temperatures. Furthermore, the incorporation of photolatent bases into these networks enables precise tuning of their viscoelastic properties in response to temperature variations. Hence, we investigated selected thiol-ene resins, bearing thioester linkages and free thiol groups, using five variations of TMG-based photobase generators. The UV-induced activation of the photolatent base subsequently yields a strong guanidine base, which is able to efficiently catalyze the thiol-thioester exchange reaction. The resulting influence of the varying photobases on the material properties was investigated using FTIR, TGA, DSC and rheological measurements. Additionally, spatially controlled activation of the thiol-thioester exchange mechanism in selected areas was demonstrated through imprinting, photochemical drawing, and self-healing experiments.

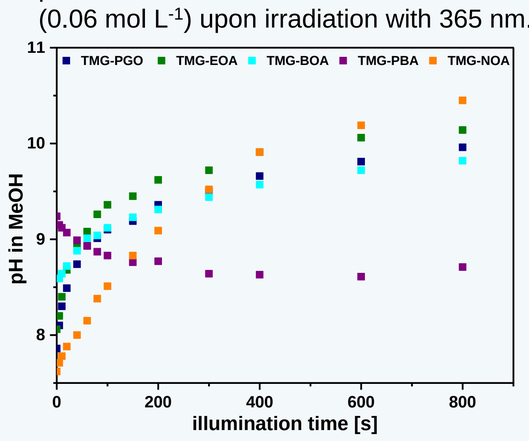


General Scheme for the manufacturing process of the dynamic thiol-ene network: Curing of the formulation between two glass slides using 450 nm UV-light followed by a spatial activation (365 nm UV-light) of the photolatent base and thermally activated thiol-thioester exchange.

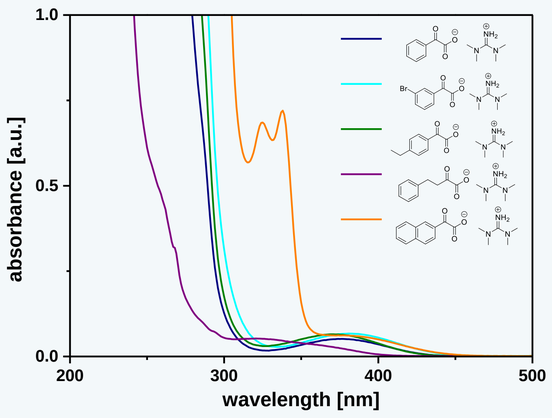
PHOTOCHEMICAL DRAWING



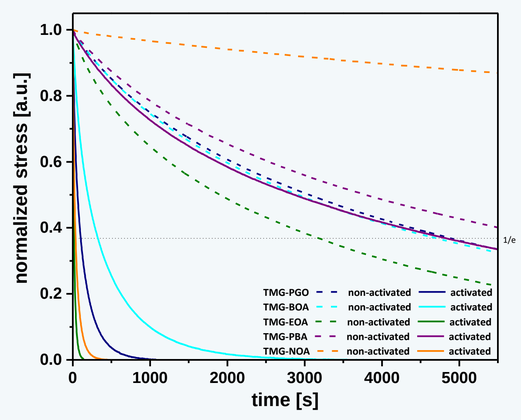
pH measurements of TMG-PLBs in methanol (0.06 mol L^{-1}) upon irradiation with 365 nm.



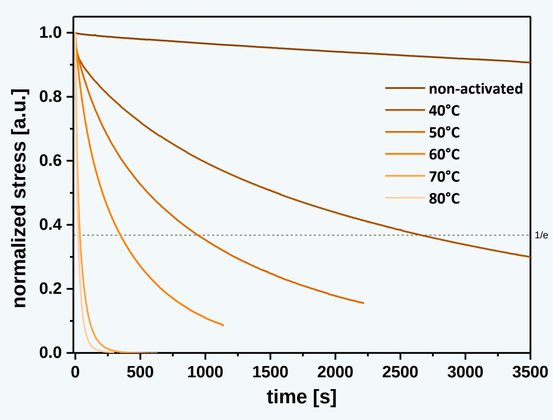
UV-Vis absorption spectra of TMG-PLBs 1 x 10^{-3} mol L^{-1} in acetonitrile.



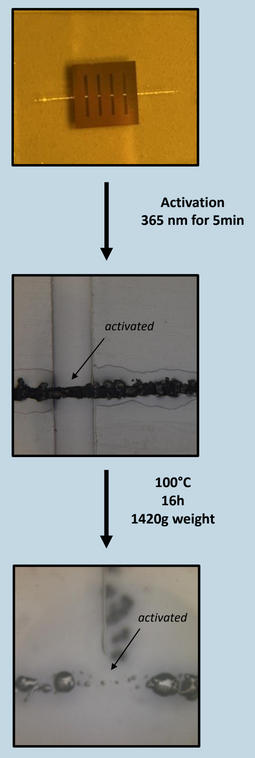
Normalized stress relaxation curves of the activated and non-activated networks at 70°C.



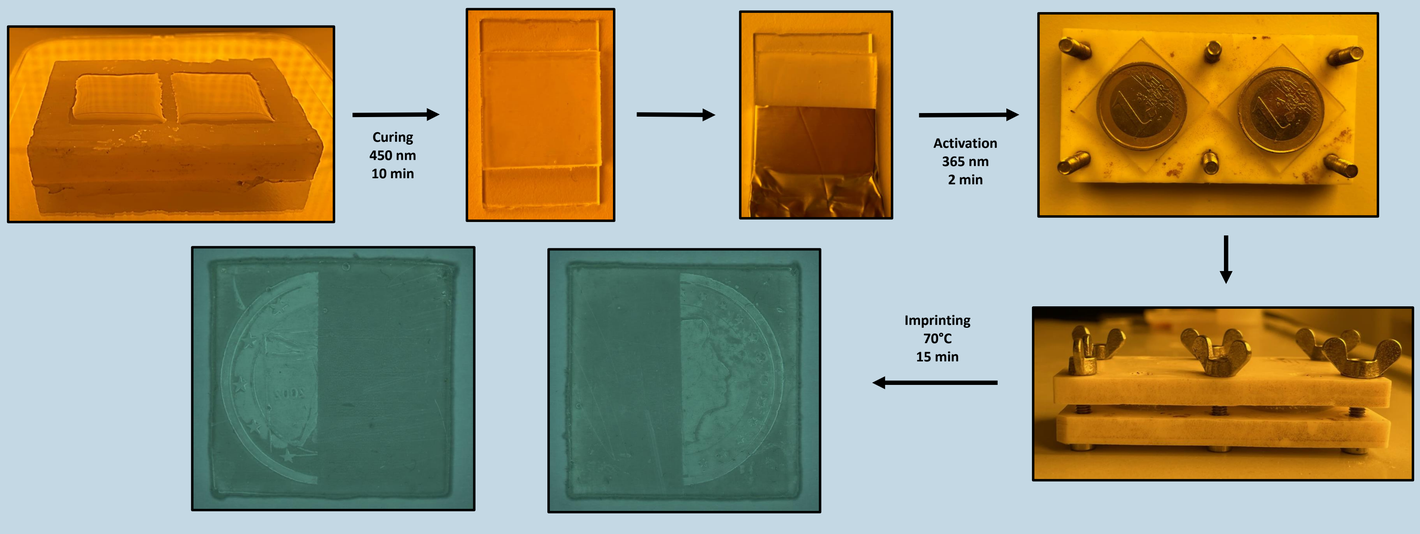
Normalized stress relaxation curves of the network containing TMG-NOA at 40-80°C.



SELF HEALING



IMPRINTING



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