FUNCTIONAL PHOTOPOLYMERS WITH DYNAMIC COVALENT BONDS

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Dynamic covalent bonds endow polymer networks with advanced functions such as self-healability, recyclability, malleability and shape memory. Current research is geared towards the design of vitrimers, which rely on thermo-activated exchange reactions such as the catalyzed transesterification of hydroxyl ester moieties. Herein, we combine the dynamic nature of vitrimers with the advantages of photo-reactive and photo-responsive polymers to expand their functionality.

Photo-labile chromophores such as *o*-nitrobenzyl esters render vitrimers photopatternable, whilst the thermo-activated topological rearrangements (and the related viscoelastic reflow) of the dynamic networks efficiently erase the structures. This enables a writing, erasing, and rewriting of micropatterns into the same region of thin vitrimer films [1].

To date, digital light processing (DLP) 3D printing of vitrimers is challenging as conventional transesterification catalysts are poorly soluble and compromise on cure rate and pot life of photocurable resins. To overcome these limitations, we introduced organic phosphates and phosphonates as a new type of transesterification catalysts. By appropriate network design, we were able to 3D print thiol-click and acrylate vitrimers with triple-shape memory and thermal mendability [2].

Advancing from thermal catalysts, we applied photolatent transesterification catalysts to conveniently switch on and locally control topological rearrangements in vitrimer networks. By exploiting two orthogonal photoreactions, a thiol-acrylate photopolymer was cured upon long-wavelength irradiation, whilst in a subsequent step, the photolatent transesterification catalyst was activated upon short-wavelength irradiation. Soft active 3D structures, which were able to undergo locally programmable shape change and malleability, were fabricated with a dual-light DLP printer.

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[1] Giebler, M., Alabiso, W., Wieser, V., Radl, S., & Schlögl, S. (**2020**). Photopatternable and Rewritable Epoxy-Anhydride Vitrimers. Macromolecular Rapid Communications, 42(2), 2000466.

[2] Rossegger, E., Höller, R., Reisinger, D., Strasser, J., Fleisch, M., Griesser, T., & Schlögl, S. (**2020**). Digital light processing 3D printing with thiol–acrylate vitrimers. Polymer Chemistry, 12, 639 – 644.