

USING ORTHOGONAL PHOTOREACTIONS TO LOCALLY CONTROL DYNAMIC BOND EXCHANGE REACTIONS

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Using light to control structural/mechanical properties and the formation of polymers is one of the most powerful tools in polymer science. It enables the production of specific, adaptable and reliable polymers and can be used for the formation, degradation and functionalization of polymers. Moreover, we have shown in our recent work that it allows to locally introduce dynamic properties into photopolymer networks. Photolabile catalysts are a versatile concept to spatiotemporally control the rate of bond exchange reactions in dynamic polymer networks at increased temperatures. The usage of photoacid generators as latent transesterification catalysts leads to the local formation of Brønsted acids upon UV exposure, which can efficiently catalyze thermo-activated transesterification reactions. By utilizing a dual-wavelength 3D printer (operating at 405 and 365 nm) the orthogonality between the curing (405 nm) of a thiol-acrylate photopolymer and the activation reaction of the catalyst (365 nm) (Figure 1) was exploited.[1, 2] This enabled the fabrication of soft active devices, which undergo locally controlled topology rearrangements at elevated temperatures and also the preparation of positive toned photoresists. More recently, the concept of chemical amplification was used to control the dynamic behavior in thiol-ene networks. Therefore, photolabile sulfonic acids were synthesized to catalyze the deprotection reaction of a tert-butoxycarbonyl group, which was introduced to mask the hydroxy groups of a vinyl monomer.[3] Simultaneously, the formed acid served as a catalyst for thermo-activated exchange reactions between the deprotected hydroxyl and ester moieties in an orthogonally-cured (450 nm) thiol-ene photopolymer.

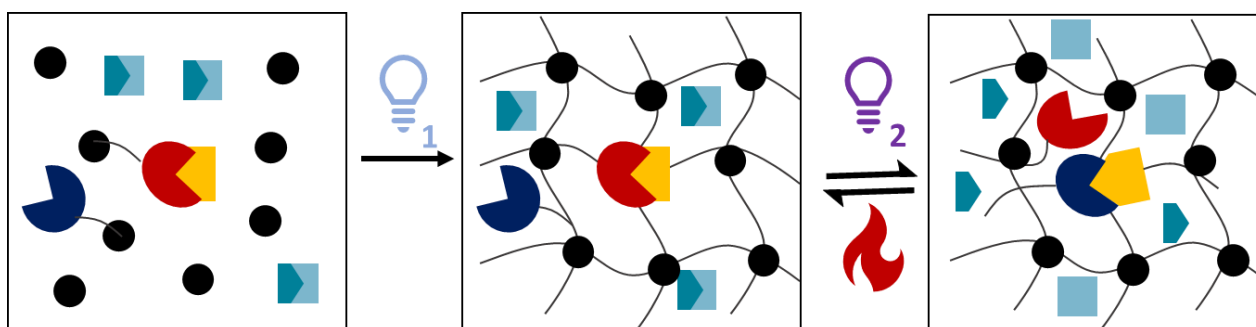


Figure 1. Orthogonality between network formation and catalyst activation to allow dynamic bond exchange.

References

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