Controlling Curing Kinetics in Thiol-ene Photopolymerization via Wavelength-Orthogonal Antagonistic Photochemistry

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Orthogonal photoreactions have attracted growing interest in polymer chemistry over the past decade.[1] The wavelength-selective activation of chromophores enables precise spatial and temporal manipulation of material properties, particularly in lithography-based additive manufacturing.[2]
In this study, we present a strategy to control thiol-ene photopolymerization by combining two antagonistic photochemical processes activated at different wavelengths. As previously introduced by Bowman et al., basic amines retard the thiol-ene reaction under certain conditions – mostly dependent on the pKa of the thiol in comparison to the amines' conjugated acids pKa.[3] We transferred this concept to photochemically activated basic compounds to gain additional control over the thiol-ene curing reaction. Radical polymerization is initiated by a type II photoinitiator activated at 450 nm, while the inhibition mechanism is triggered by a photolatent base at 365 nm. The difference in absorption of these components allows fine-tuned modulation of the curing kinetics by the light dose used.
This approach enables precise local retardation or suppression of the curing reaction. Experiments such as laser writing and grayscale patterning confirm the resolution and versatility of this method. By integrating photochemically gated inhibition, such systems offer new capabilities in lithography-based additive manufacturing and advanced photolithography.

Keywords: antagonistic photoreactions, thiol-ene, photochemistry

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