

PHOTOPOLYMERIZATION AND LIGHT-INDUCED PROGRAMMING OF COVALENT ADAPTIVE SEMI-CRYSTALLINE NETWORKS

Alexa S. Kuenstler^a, Juan J. Hernandez^a, Alina M. Martinez^b,
and Christopher N. Bowman^{a,b}

^aDepartment of Chemical and Biological Engineering, University of Colorado Boulder,
Boulder, Colorado 80309, United States

^bMaterials Science and Engineering Program, University of Colorado Boulder, Boulder,
Colorado 80309, United States

Recent advances in materials chemistry have enabled the incorporation of dynamic covalent bonds within photopolymerized networks. Such bonds enable reconfigurability and recyclability of crosslinked networks, and their inclusion via photopolymerization introduces unprecedented control over the geometry and responsiveness of polymer constructs. However, accessing the materials properties such as large extensibility, toughness, and elastic modulus required for many applications remains a challenge both within dynamic covalent networks and photopolymerization-based additive manufacturing. In this work, we introduce a method to incorporate thioester bonds within photopolymerizable semi-crystalline networks via thiol-ene chemistry. In the presence of catalytic nucleophiles, these materials can rapidly relax stress through a thiol-thioester exchange mechanism that can be tailored through the choice of stoichiometry, catalyst, and network chemistry. Furthermore, semi-crystallinity makes these materials strong and tough elastomer, while bond exchange can be exploited to facilitate programmed anisotropy and shape-memory. Additionally, excess thiol can be used to fully degrade these materials into oligomers that can be reprocessed into new materials, thus introducing recyclability into high-performance thermosets. Finally, we show that these materials are amendable to digital light processing-based additive manufacturing. Using this fabrication method, we demonstrate the printing of complex structures with exceptional material properties that can be reconfigured and recycled.