

## Photocrosslinking Enabled by 1,2-Dithiolanes for Dynamic and Responsive Materials

Benjamin R. Nelson<sup>1,2</sup>, Bruce E. Kirkpatrick<sup>1,2</sup>, Marianela Trujillo-Lemon<sup>1</sup>, Jaxon Cione<sup>1</sup>, Kristi S. Anseth<sup>1,2,3</sup>, Christopher N. Bowman<sup>1,3</sup>

<sup>1</sup>Department of Chemical and Biological Engineering, University of Colorado Boulder,

<sup>2</sup>BioFrontiers Institute, University of Colorado Boulder,

<sup>3</sup>Materials Science and Engineering Program, University of Colorado Boulder

The design of materials that possess characteristics of both thermoplastics and thermosets has played a pivotal role in transforming conventional polymeric materials. By employing covalent adaptable networks (CANs), the mechanical benefits of crosslinked materials such as toughness and dimensional stability can be effectively blended with the self-healing and reprocessing capabilities associated with non-crosslinked thermoplastics. Seeking to expand on the chemistries used for the deployment of dynamic covalent bonds in networks, we utilize 1,2-dithiolanes, a ring strained cyclic disulfide, for the photopolymerization of CANs. These molecules have been long known to undergo ring opening polymerizations, but their applications in materials have been limited until recently.<sup>[1]</sup> This ring opening reaction of the dithiolanes directly results in the dynamic linear disulfide moiety at the crosslink.<sup>[2]</sup> Because of the ring strain, these moieties absorb light and are inherently photoreactive, and thus are capable of polymerization with or without exogenous initiator.<sup>[3]</sup> The resulting disulfide bonds are capable of multiple actions and respond to varied stimuli. Using dithiolane-functionalized monomers, we form disulfide crosslinks under mild conditions through the photoinduced ring-opening polymerization. These versatile materials present another addition to the CANs toolbox for smart, stimuli responsive materials.

### References

- [1] J. A. Barltrop, P. M. Hayes, M. Calvin, in *Journal of the American Chemical Society*, Vol. 76, American Chemical Society, 1954.
- [2] X. Zhang, R. M. Waymouth, in *Journal of the American Chemical Society*, Vol. 139, American Chemical Society, 2017.
- [3] B. R. Nelson, B. E. Kirkpatrick, C. E. Miksch, M. D. Davidson, N. P. Skillin, G. K. Hach, A. Khang, S. N. Hummel, B. D. Fairbanks, J. A. Burdick, C. N. Bowman, K. S. Anseth, *Adv Mater* 2023, e2211209.