PHOTOPOLYMERIZATION IN COVALENT ADAPTABLE NETWORKS

Christopher Bowman[1,2]

[1] Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado80309, United States

[2]Materials Science and Engineering Program, University of Colorado Boulder, Boulder, Colorado80309, United States

Pursuit of materials to meet the needs of emerging technologies, however, has led to the development of polymers with pre-engineered, non-permanent linkages holding them together. Dynamic covalent chemistries (DCC), coupling reactions or functional groups that exhibit the ability of either reversible addition or reversible exchange, can be incorporated into polymers to provide the capability to respond to exogenous or endogenous signals.

When applied within crosslinked polymers, these materials (designated covalent adaptable networks or CANs) may adopt many of the advantages of thermoplastics (e.g. processability, recyclability) while maintaining those advantages of crosslinked polymers (e.g. high strength). User control over CANs extends further than that when DCCs are combined with other modes of responsiveness in materials such as shape memory or liquid crystal alignment, resulting in materials that change modulus, shape, size, color, etc. upon exposure to multiple selective stimuli, either sequentially or simultaneously.

Photopolymerization and photochemistry more generally have been employed in the creation and manipulation of CANs via several overlapping strategies. Photopolymerization provides a means for curing CANs. The Bowman group has used photomediated radical chain addition, thiol-ene, Michael addition, Huisgen cycloaddition, disulfide exchange and other reactions to generate CANs. Further, the DCCs themselves, and not only the polymerization, may be photomediated. The Bowman groups has used photolatent acids and bases to control base-catalyzed thiol-thioester exchange in networs and has used radical photoinitators to drive bond exchange in disulfides, allyl sulfide, and trithiocarbonate within CANs. Finally, the availability of photomediated reactions with varying mechanisms allows employment of DCCs in multistage polymerized materials capable of responding independently to multiple, orthogonal stimuli, enabling design and development of ever smarter smart materials.

The toolbox of photopolymerization and photomediated dynamic chemistries is extensive and expanding, indicative of broad interest in their research and applications. PhotoCANs hold potential to address needs in fields as diverse as optical devices to additive manufacturing to biomedicine through the development of materials capable of otherwise unachievable characteristics.