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Chemically Recyclable Crosslinked Thiol-Based Polymers Via Thiol-Disulfide Exchange Reactions

Background

Photopolymers are generated from a mixture of photoreactive liquid monomers or oligomers that can solidify upon irradiation of light. These materials exhibit fast reaction kinetics, solvent-free processes, and tunable material properties, which make them attractive for industrial applications. Photopolymers used in industrial applications are often covalently crosslinked to ensure good chemical and solvent resistance as well as robust thermal and mechanical properties.

There have been recent developments in covalent adaptive networks (CANs), which contain reversible or dynamic linkages that can remain connected under normal service conditions. When exposed to external stimuli, these linkages can cleave or undergo bond exchange, which allows the materials to have self-healing and re-processing/recycling capabilities.

There has been some research on incorporating CANs into crosslinked photopolymers to make them re-processable or recyclable. However, current methods typically require multi-step pre-syntheses of the photoreactive building blocks that contain desired dynamic linkages or functionalities.

Invention Description

Researchers at Arizona State University have developed a novel method for synthesis of a chemically recyclable crosslinked photopolymer containing dynamic disulfide linkages. The synthesis method uses thiol-ene photopolymerization reactions between liquid polysulfides, which contain both reactive thiol end groups and internal disulfide bonds, as well as multifunctional alkenes. This method allows for complete degradation via thiol-disulfide exchange reactions upon the addition of excess free thiol groups and a base catalyst. The degraded oligomer mixture of thiol-groups can later be re-crosslinked with multifunctional alkenes under the same conditions as the starting material, and retain similar chemical compositions and material properties.

Potential Applications

- Improved sealants
- Additive manufacturing (3D printing)
- Enhanced fiber materials
- Biomaterials/dentistry

Benefits & Advantages

- Eliminates tedious pre-syntheses processes required by previous methods
- Enables examination of thiol-disulfide exchange reactions on resulting networks
- Uses commercially available chemicals & materials
- Can be potentially recycled multiple times without loss of material properties
- Can portray different material properties by modifying the building block while maintaining chemical recyclability

Related Publication: "Chemically recyclable crosslinked thiol-ene photopolymers via thiol-disulfide exchange reactions" | Journal of Polymer Science (2022).