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Thesis abstract

The application of photomediated RAFT polymerisation in 3D printing

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Vat photopolymerisation (VP) is a promising additive manufacturing technology which enables the construction of complex 3D objects via versatile photochemistries. VP techniques have demonstrated superior advantages in imparting spatiotemporal control and providing high build rates and high printing resolution. However, current photocuring methods are based on non-living free radical or cationic polymerisation which offer limited control over chain growth, network formation, and thus the final properties of 3D printed materials. Moreover, inert polymer chains produced during the polymerisation are incapable of being reactivated for post-functionalisation of pre-formed polymers. To fabricate materials with controlled properties and post-modifiable networks, photomediated Reversible Addition-Fragmentation chain Transfer (RAFT) polymerisation techniques were employed in VP. The addition of RAFT agents in photoresins provided control over polymer chain growth and network formation. Also, the retention of thiocarbonylthio polymer chain-ends in the network imparted living characteristics to 3D printed materials, which were easily post-modified with diverse functions and properties.

This work firstly explored photoinduced electron/energy transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerisation in 3D printing under visible light irradiation in the open air. The use of an organic dye in conjunction with a tertiary amine as co-catalyst allowed fast printing speeds. The inclusion of RAFT agents in photoresins provided control over the mechanical properties of 3D printed materials. The presence of latent RAFT agents in the resin allowed post-functionalisation of these materials. Based on this study, photoresins containing RAFT agents with different activating Z groups and leaving R groups were investigated for their application in 3D printing. Also, the impact of the concentration of trithiocarbonates on mechanical properties of 3D printed materials was demonstrated. In addition, the 3D printed materials containing RAFT agents were easily post-modified via one-pot in situ aminolysis and thiol-Michael additions. Finally, the inclusion of RAFT agents in 3D printed thermoset materials conferred self-healing functionality. Materials containing trithiocarbonate units that were 3D printed under visible light can perform rapid self-repair via a secondary polymerisation mechanism under UV light irradiation under open-air conditions and at room temperature. This study promisingly paves the way for the fabrication of novel 3D printed thermosets with self-healing properties.

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