

SEEING THE LIGHT: ADVANCING MACROMOLECULAR SYNTHESIS FOR 3D PRINTING AND SURFACE FUNCTIONALIZATION

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Reversible addition-fragmentation chain-transfer (RAFT) polymerization is a valuable tool for synthesizing macromolecules with controlled topologies and diverse chemical functionalities.¹ However, the application of RAFT polymerization to additive-manufacturing processes has been prevented due to the slow polymerization rates of typical systems. In this oral presentation, we developed a rapid visible light mediated RAFT polymerization process and applied it to a 3D printing system.² The photosensitive resins contained a metal-free dye (erythrosin B) in conjunction with a tertiary amine co-catalyst (triethanolamine) and a trithiocarbonate RAFT agent (2-(butylthiocarbonothioylthio) propanoic acid) to afford polymerization without prior deoxygenation. The reaction components are non-toxic, metal free and environmentally friendly (water based photosensitive resin), which tailors these systems toward the fabrication of biomaterials. Following optimization of the resin formulation by varying the ratio of photocatalyst and tertiary amine, a variety of 3D printing conditions were investigated to prepare functional materials using green light ($\lambda_{\text{max}} = 525 \text{ nm}$, $I_0 = 0.32 \text{ mW/cm}^2$). Furthermore, the mechanical properties of these 3D printed materials were tested under different conditions. Interestingly, the concentration of trithiocarbonate impacted the mechanical properties and the performance of these materials. Remarkably, the use of a photoinduced polymerization process provided facile spatial control over the network structure by varying the light dose to each layer of the 3D printed material; using this strategy, a 4D printing process was demonstrated via 3D printing and subsequent swelling and dehydration induced actuation. Furthermore, the trithiocarbonate species incorporated in the polymer networks were able to be reactivated after the initial 3D printing process, which enabled post functionalization of the printed materials via secondary photopolymerization processes. This RAFT-mediated 3D and 4D printing process should provide access to a range of new functional and stimuli-responsive materials.

[1] a) C. Wu, N. Corrigan, C.-H. Lim, K. Jung, J. Zhu, G. Miyake, J. Xu, C. Boyer, *Macromolecules* 2019, 52, 236-248; b) C. A. Figg, J. D. Hickman, G. M. Scheutz, S. Shanmugam, R. N. Carmean, B. S. Tucker, C. Boyer, B. S. Sumerlin, *Macromolecules* 2018, 51, 1370-1376; c) S. Shanmugam, S. Xu, N. N. M. Adnan, C. Boyer, *Macromolecules* 2018, 51, 779-790.

[2] a) Z. Zhang, N. Corrigan, A. Bagheri, J. Jin, and C. Boyer, *Angew. Chem. Int. Ed.*, 2019, DOI: 10.1002/ange.201912608; b) X. Shi, J. Zhang, N. Corrigan, C. Boyer, PET-RAFT facilitated 3D printable resins with multifunctional RAFT agents. *Materials Chemistry Frontiers* 2021, DOI: 10.1039/D0QM00961J; c) K. Jung, N. Corrigan, M. Ciftci, J. Xu, SE Seo, C. Hawker, C. Boyer, *Adv. Mater.* 2020, 32, 1903850. <https://doi.org/10.1002/adma.201903850>