



Living Additive Manufacturing

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Living organisms such as bacteria are able to grow, respond to stimuli, and divide as part of their life cycle. Designing smart three-dimensional (3D) materials that are able to perform such feats, i.e., continue on-demand growth and respond to external stimuli, is always a challenge for polymer and material scientists. At present, Johnson and co-workers have made a significant step forward in this field by the design of an approach capable of growing and replicating gels.¹

Current photomediated additive manufacturing, a commonly used technique for 3D printing, relies on free radical polymerization techniques via layer-by-layer addition or continuous solid–liquid interface production of polymers. Both techniques result in the formation of “dead polymers” which are unable to be further chain extended to introduce new functionalities in a living manner. Johnson and co-workers¹ engineered an alternative approach where a 3D “parent” gel is able to grow, respond to stimuli, and even generate a “daughter” gel that mimics or has completely diversified chemical and mechanical properties using visible light. In this light-mediated approach for additive manufacturing, a “living parent” gel is first fabricated, and the subsequential addition of functional monomers/cross-linkers is used to grow next generation of “daughter” gels with exceptional spatiotemporal control through photocatalysis, a field that recently has been gaining momentum.^{2–6}

In their previous work, Johnson and co-workers reported on the use of the photoredox catalyst 10-phenylphenothiazine (PTH) to mediate solution polymerization of acrylate and acrylamide.⁷ In the current work, photoredox catalyzed growth (PRCG) of uniform polymer gels is first designed by forming a network of homogeneous polymers via strain promoted alkyne–azide cycloaddition (SPAAC) of a four-arm polyethylene glycol (PEG) star polymer with dibenzocyclooctyne (Tetra-DBCO-PEG) and a bis-azide trithiocarbonate (bis-N₃-TTC) in the presence of monomer, PTH, and/or cross-linker. Under blue light irradiation, PTH activates photo-RAFT polymerization, which results in monomer insertions to expand the network strands.

Boyer on results that get us closer to materials with life-like properties reproduction.

In contrast to conventional photo controlled/living radical polymerization, which employs a photoinitiator, Johnson’s approach employs a photocatalyst which regulates the RAFT polymerization, via a reversible photoinduced electron transfer between the RAFT and photocatalysts—known as photoinduced electron/energy transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerization. The ability to reversibly activate and deactivate confers remarkable living properties to the polymers, and therefore to the gels. The novelty of this approach stems from the fact that chemically and mechanically differentiated or similar daughter gels can be derived from a single parent gel by manipulating parameters such as the polymer chain length, cross-linking density, and composition of the polymer network. For instance, a softer or stiffer daughter gel in comparison to the parent gel can be made by adding or removing cross-linkers. In addition, by maintaining constant cross-linking densities, daughter gels with different compositions are found to have similar mechanical properties. By using monomers such as *N*-isopropylacrylamide, *n*-butyl acrylate, and poly(ethylene glycol) methyl ether acrylate, thermal as well as polarity responsiveness can be introduced in the daughter gels. The daughter gels are able to self-heal after damage with improved mechanical properties. Daughter gels of similar and different compositions can be welded together to form complex gel progeny with spatially different compositions (Figure 1).

The current living additive approach developed by Johnson and co-workers is able to dictate the length, distribution, as well as composition of the final gel polymer products which has never been possible with previous additive manufacturing techniques. Nevertheless, as noted by

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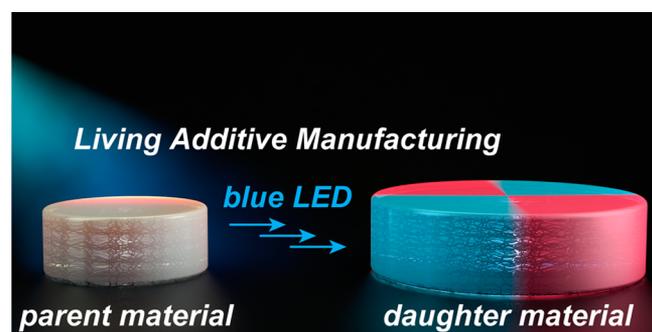


Figure 1. Photoredox catalyzed growth can be used to synthesize daughter materials of defined and divergent properties compared to the parent material. Credit: Jeremiah Johnson and Demin Liu.

The novelty of this approach stems from the fact that chemically and mechanically differentiated or similar daughter gels can be derived from a single parent gel by manipulating parameters such as the polymer chain length, cross-linking density, and composition of the polymer network.

the authors, this discovery is still in the preliminary stages, and further optimizations are required before adapting it for commercial applications such as 3D printing. Current 3D printing developed by DeSimone and co-workers⁸ is not only able to print parts in a matter of minutes but also uses oxygen, which is often an inhibitor for complete cure, to create “dead zones” for continuous liquid interface production (CLIP) of 3D objects. In order for the PRCG approach to be adapted for 3D printing, researchers must overcome its current lack of oxygen tolerance and slow polymerization rates (a matter of hours). In addition, as PET-RAFT polymerization is the core chemistry for building the daughter gels, recent innovations, such as stereoregulation⁹ and sequence control,¹⁰ can be synchronized with this approach in order to build gels with greater complexities and functions especially when it comes to designing hydrogels that mimic the intricate microenvironment of cells.¹¹ A recent study by Hawker and co-workers has shown the distinct physicochemical properties of molecularly defined oligomer in comparison to disperse or polydisperse oligomers.¹² Another avenue to diversify the chemical and mechanical properties of the daughter gels will be utilizing PRCG approach to generate structurally uniform polymers instead of relatively dispersed polymers.

Although the development of the PRCG approach is still at an infancy stage, this technology does have the great potential to become a fundamental approach in

generating materials for both biomedical and advanced applications.

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Notes

The authors declare no competing financial interest.

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