

Chemical Engineering Thesis Defense

Rapid Water Tolerant Cationic RAFT Photopolymerization

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Abstract

In the search for ever more sustainable manufacturing techniques, additive manufacturing through light driven 3D printing processes is growing rapidly as a field, specifically the production of “living” materials which can be repaired and or reprocessed through the reactivation of polymer chain ends. Currently research in the production of these living materials is largely focused on radical polymerization methods. Cationic polymerizations have been developed for this purpose, although there is still much work to be done. This work seeks to explore a transition-metal free system to produce living materials through cationic reversible addition fragmentation chain-transfer (C-RAFT).

Cationic polymerization is known for its rapid propagation. This is due to the highly reactive active center which also readily reacts with nucleophiles in unwanted chain transfer reactions. For this reason, reagents in living cationic polymerizations are subject to rigorous purification steps involving the distillation of monomer and solvent, freeze—pump—thaw cycles, and running the reaction under an inert environment . These restrictions make living cationic polymerizations unattractive for 3D printing processes. New systems for rapid water tolerant C-RAFT photopolymerization will provide for new materials to be produced through this more sustainable manufacturing process.

In this work, living cationic polymerization of isobutyl vinyl ether (IBVE) is achieved using a synthesized cationic RAFT agent and an initiating system consisting of camphorquinone (CQ), ethyl 4-(dimethylamino)benzoate, and iodonium salt HNu-254. Molecular weights of 12 kg/mol are achieved with a dispersity of 1.4. The polymerization mechanism is probed and shows rapid kinetics consistent with living polymerizations in addition to photo-controllability as indicated by light on-off experiments. Chain extension experiments display re-activation of the trithiocarbonate chain end. This feature is then used to produce block-copolymers using ethyl vinyl ether and cyclohexyl vinyl ether.

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