

Polymer and Colloid Highlights

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Near-Quantitative, Catalyst-Free Depolymerization of RAFT Polymethacrylates

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Controlled radical polymerization (CRP), also known as reversible deactivation radical polymerization, is an advanced variation of free radical polymerization that enables the synthesis of vinyl polymers with tunable molecular weight, dispersity, architecture.^[1] The key feature of CRP that enables such control is the chemical moiety located at the chain-end. This end-group can be activated in various ways (*e.g.* with a catalyst, radical, or light) and ultimately endow control over the polymerization.

However, because CRP operates via radical addition across a π -bond, the resultant polymer has a backbone comprising purely of stable C–C σ -bonds that are highly unreactive. This stable backbone makes it difficult to undo the polymerization (*i.e.* depolymerize the polymer back into its monomers) without the use of highly energy-intensive reaction conditions (>400 °C).^[2] The difficulty in reversing CRP is exemplified by the huge asymmetry between the volume of publication on the topic of polymerization and depolymerization.

In our recent work,^[3] we utilized the high end-group fidelity of polymethacrylates synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization to near-quantitatively depolymerize various bulky and non-bulky (functional) polymethacrylates without the use of a catalyst (Fig. 1). We found that, under the optimal concentration and temperature, a chain-end radical is produced, leading to the rapid depolymerization of these polymers (Fig. 2a,b). In the absence of the RAFT end-group, negligible depolymerization was observed, highlighting the importance of end-group. In addition to near-quantitatively regenerating the monomer, the cleaved end-group could be reused to mediate a subsequent RAFT polymerization of the regenerated monomer (Fig. 2c,d).

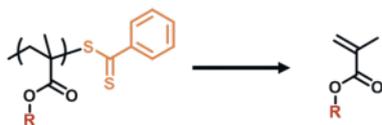


Fig. 1. Schematic of the depolymerization of polymethacrylates synthesized by RAFT polymerization.

Overall, these results exploit the high end-group fidelity of RAFT polymethacrylates to near-quantitatively regenerate the monomer in a catalyst-free manner. This work shines light on another advantage of RAFT polymerization and further develops the field of depolymerization.

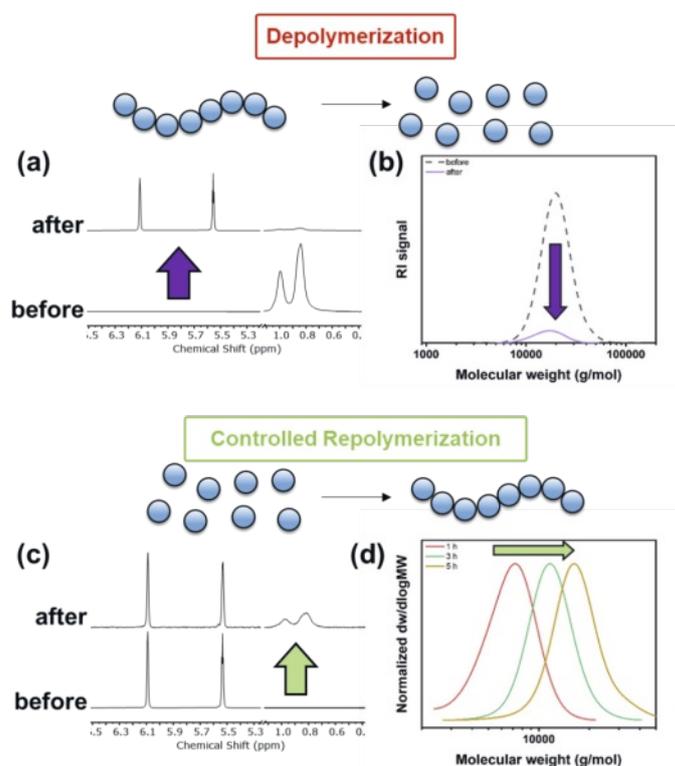


Fig. 2. (a) Nuclear magnetic resonance spectroscopy and (b) size-exclusion chromatography traces of poly(oligo(ethylene glycol methyl ether methacrylate)) before and after depolymerization. (c) Nuclear magnetic resonance spectroscopy and (d) normalized size-exclusion chromatography traces of the subsequent repolymerization reaction.

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