Degradable Polymers via Catalytic Living ROMP

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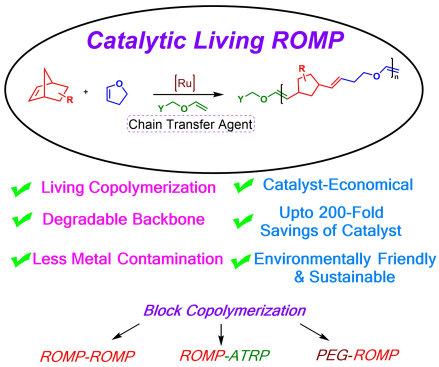
The development of degradable polymers has commanded significant attention over the past half-century. [1] Since most of the metathesis polymers lack backbone degradability, recent efforts have been directed toward expanding the family of degradable polymers accessible via olefin metathesis polymerization for their potential applications in drug delivery, therapeutics, technology as well as for environmental sustainability. Although several routes have been developed to synthesize degradable polymers via ring-opening metathesis polymerization (ROMP), they all rely on the utilization of stoichiometric amounts of ruthenium-based metal catalysts, which bestow a ruthenium carbene on each polymer chain during the polymerization. This often results in high catalyst loading, which is quite expensive and leads to toxic metal contaminants in the synthesized polymers, potentially hindering the industrial and biomedical applications of these materials. The design of ROMP methods that require only a catalytic amount of ruthenium catalyst is desirable to realize lower costs and the most sustainable syntheses compared with ROMP using a traditional amount of catalyst. But, finding a catalytic ROMP protocol that will facilitate the synthesis of living and degradable polymers has always been a challenging issue. Herein, we have demonstrated a new catalytic living ROMP mechanism exploiting the regioselectivity and high metathesis activity of vinyl ethers as chain transfer agents (CTAs) to synthesize narrowly dispersed degradable polymers by copolymerizing 2,3-dihydrofuran (DHF) with several norbornene derivatives.[2,3] All characteristics of a living polymerization such as narrow dispersity, excellent molar mass control, and the ability to form block copolymers are achieved by this method. This simple and one-pot approach allows the use of up to 200 times less ruthenium complex than traditional living ROMP. Narrowly dispersed ROMP-ROMP diblock copolymers, ATRP from a ROMP macro-initiator, and living ROMP from a PEG-based macro chain transfer agent were also synthesized quite straightforwardly by this strategy. We believe that this cost-effective, sustainable, and environmentally friendly synthesis of degradable polymers and block copolymers enabled by this method will find various applications in bordering fields.



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