Controlled Ring-Opening Polymerization for Functionalized Cyclic Poly(α-Hydroxy Acids) with Improved Thermal-Mechanical Properties

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Polymer topology markedly affects material properties. Cyclic polymers exhibit distinct properties due to the end-free structure, including reduced hydrodynamic volumes, higher T_g, and lower intrinsic viscosities (η) compared to linear counterparts. While high molecular-weight (MW) petrochemical-based cyclic polymers can be synthesized via ring-expansion polymerization, controlled synthesis of degradable cyclic polyesters remains challenging due to side reactions such as linear enchainment, chain transfer, and epimerization. Synthesizing functionalized cyclic poly(α-hydroxy acid) (PAHA) with high MWs (>100 kDa) and narrow distributions ($Đ < 1.2$) continues to be elusive despite extensive research on cyclic poly(lactic acid). Furthermore, the sequential monomer addition for cyclic block copolyester synthesis remains largely unexplored, contrasting with the well-established methods for linear block copolyesters.

Herein we developed a controlled ring-opening polymerization (ROP) of *O*-carboxyanhydrides (OCAs) using a sterically optimized lanthanum complex with a C_2-symmetric bis(oxazoline) ligand (**La-1**, Fig.1A-B). Combined with a redox-active **Mn-1** complex for decarboxylation, we achieved rapid polymerization completed in 0.5 h, affording a polymer with a M_n of 58.4 kDa and a $Đ$ of 1.04. SEC analysis confirmed the cyclic topology of *c*-poly(**1**), characterized by later elution time, lower radius of gyration (R_g), and reduced η compared to linear analogs. The polymerization exhibited living characteristics with a linear MW-conversion correlation and first-order kinetics.

Furthermore, sequential monomer addition enabled one-pot synthesis of cyclic block copolymers with precise control of M_n and $Đ$ (Fig. 1C). The formation of block copolymers was confirmed by single diffusion coefficients in DOSY NMR.

Lastly, our cyclic PAHAs, particularly block *c*-poly(**1**-*b*-**4**) comprising glassy and soft segments, had enhanced mechanical properties including improved strength and toughness compared to their linear analogs (Fig. 1D). The unique properties of cyclic PAHAs position them as promising materials for biomedical and packaging applications (*Angew. Chem.* 2025, e202423973).

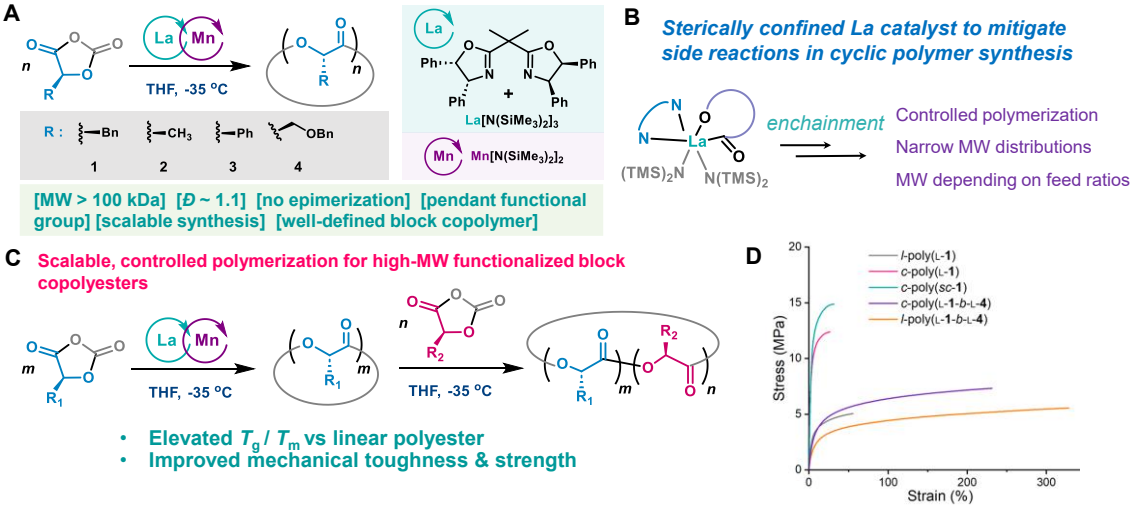


Figure 1. Controlled ROP for degradable cyclic PAHAs.