PROJECT POLYBIO: Chain-Shuttling **Poly**merization of **Bio**-Sourced Monomers

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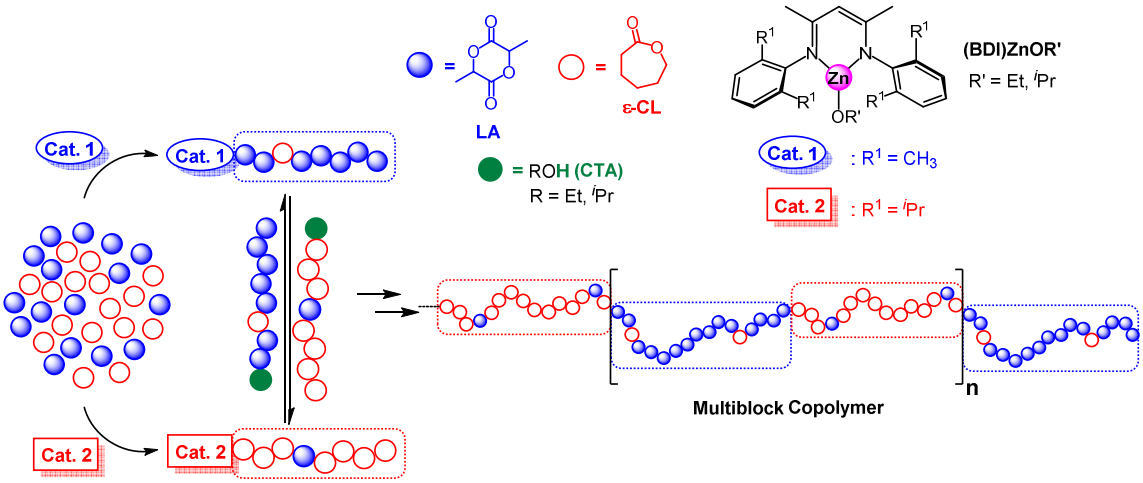
Polylactide (PLA) is currently considered as the major polymer as potential substitute of widely used petroleum-based plastics.[1] It is typically produced by coordination polymerization (Ring-Opening Polymerization,[2] ROP) of the cyclic ester LA, a dimer of lactic acid, which is extracted from biomass via biotechnological processing. However, PLA has limitations to pretend to compete with conventional plastics and their great variety of properties, in particular a brittle behavior, poor elasticity, low thermal stability and other disadvantages that limit the range of its potential applications.[3] To overcome this problem, many efforts have been devoted to the preparation of di-, tri-block and random PLA-based copolymers (mainly with ε-caprolactone, ε-CL, as comonomer), however, only few reports have described the synthesis of counterparts having a multiblock PLA-based copolymer architecture.

In the present project, we propose an original approach based on coordination catalysis by reversible cross chain transfer, also called Chain Shuttling Polymerization (Scheme 1),[4] in order to afford multiblock PLA-PCL copolymers with precise control over comonomers distribution and homo-sequence lengths.



Scheme 1: Multi-sequenced polymers chains growing by Chain Shuttling Polymerization

To achieve these ends, we will prepare a series of zinc complexes supported by β-diketiminate (BDI) ligands (Scheme 1) that display high activity toward the ROP of cyclic ester.[5] We will pay particular attention on the choice of the BDI ligand framework encompassing different steric properties, as sterically hindered metal-based initiators are expected to favor the insertion of the least bulky comonomer, ε-CL (and disfavor that of bulkier comonomers, LA).[6]

This project is focusing on coordination chemistry, organometallic catalysis (homogeneous medium) and polymer chemistry. Experience in organic synthesis and air-sensitive metal-based complexes will be appreciated (Schlenk technique, glove box, characterization by NMR).

Time period: 6-9 months

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