Polymerization of Heterocycles using Organometallic Complexes: a Simple Approach to Sequence Control in Polymer Synthesis

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There are economic and social issues associated with the depletion of fossil feedstocks and the accumulation of conventional polyolefin plastics. Given the growing need for inexpensive biodegradable plastics for use in various applications, the development of synthetic methods for the polymerization of a wide range of monomers with control over the stereochemistry, molecular weight, and comonomer incorporation is of particular importance.[1] In this context aliphatic polyesters have emerged as biodegradable materials with huge potential.

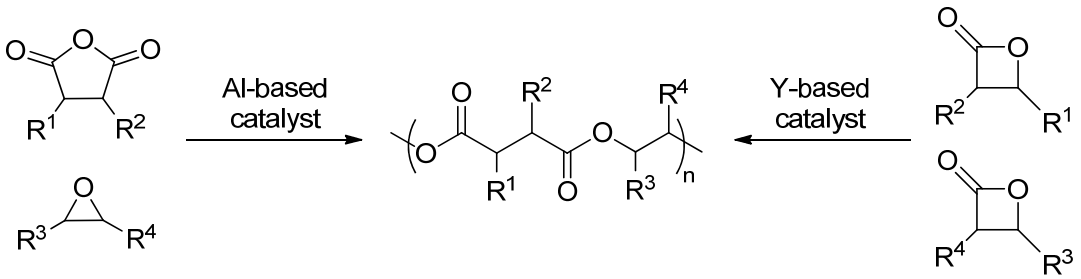

Fig. 1: Synthetic approaches to aliphatic polyesters

Recently we have synthesized new biodegradable poly(β-hydroxyalkanoate)s (PHAs) with controlled primary structures.[2] By using highly efficient yttrium complexes as initiators, we were able to synthesize highly alternating copolymers by ring-opening polymerization of a mixture of enantiomerically-pure but different monomers. This efficient catalytic system makes copolymers that would be very difficult to make through any other method. Also we have reported a new strategy to obtain biodegradable polyesters.[3] This was achieved by tandem catalysis, which confers great interest to this approach.[4] Commercially available complexes were used as efficient catalysts for cyclization of dicarboxylic acids followed by alternating copolymerization of the resulting anhydrides with epoxides. Given an operationally simple method, this tandem catalysis is an attractive strategy for the production of new renewable materials.

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[3] a) C. Robert, F. De Montigny, C. M. Thomas, *Nat*. *Commun*. **2011**, *2:586*, doi: 10.1038/ncomms1596. b) C. Robert, F. De Montigny, C. M. Thomas, *ACS*. *Catal*. **2014**, *4*, 3586-3589.
[4] C. Robert, C. M. Thomas, *Chem*. *Soc*. *Rev*. **2013**, *42*, 9392-9402.