

Noncovalent Interactions: Your Key Players in Metal-mediated Stereocontrolled Ring-Opening Polymerization of Cyclic (thio)Esters

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The preparation of stereocontrolled homopolymers and alternating copolymers is of paramount importance. Their microstructure finely dictates their properties and, hence, their possible applications. Our team has developed over the past 20 years several classes of rare-earth based catalysts for the ring-opening polymerization (ROP) of different classes of cyclic (thio)esters. The resulting polymers belong to a class of materials that receives more and more attention because of their ready (bio)degradability and potential recyclability, which make them possible alternatives to conventional “plastics” and for a circular economy.

An interesting feature of the *achiral* catalysts we have developed is that, by simply tuning the nature of one ligand substituent, they enable the preparation of polymers with different microstructures: syndiotactic or, even more uniquely, isotactic polymers starting from racemic mixtures of the chiral monomers. On the other hand, starting from mixtures of chemically different enantiopure monomers with opposite absolute configuration, original highly alternated copolymers can be accessed. The possible origins of stereoselectivity in these ROP processes will be discussed. We will highlight the close interplay between the nature of the cyclic ester, most particularly of the exocyclic functional chain installed on the chiral center of β -lactones, and the *ortho*-substituents installed on the phenolate rings of the ligand, that results in various determining secondary/non-covalent interactions (NCIs) of steric and also electronic nature.

