

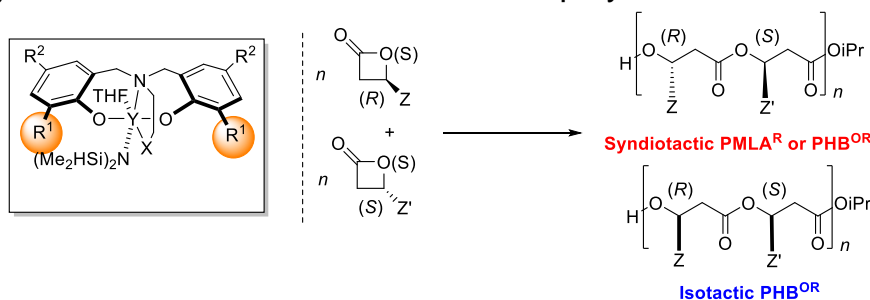
Metal-mediated Stereocontrolled Ring-Opening Polymerization of Cyclic (thio)Esters towards "Green"/Renewable Plastics

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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 15 years several classes of rare-earth based catalysts for the ring-opening polymerization (ROP) of different classes of cyclic (thio)esters.^[1] The resulting polymers belong to a class of materials that has received much attention because, thanks to their ready (bio)degradability and potential recyclability, they constitute a possible alternative to conventional "plastics" that cause so much environmental issues. 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. Examples of such microstructural tuning and attempts at rationalizing (predicting?) stereo/electronic effects that are at play will be showcased.



References:

[1] For a recent, leading reference, see: H. Li, J. Ollivier, S. M. Guillaume, J.-F. Carpentier, *Angew. Chem. Int. Ed.* **2022**, 61, e202202386. DOI: 10.1002/anie.202202386.

