

## ABSTRACT.

Aliphatic polyesters are emerging as an important class of materials alternatives to petroleum-based polymers. They are often biodegradable and can be produced from renewable feedstocks. In this context, the development of controlled polymerization routes such as the ROP of cyclic esters and the ROCOP between epoxides and anhydrides, is of high interest.

Salen complexes based on five-coordinated aluminum have been widely studied to promote the ROP of cyclic esters such as lactide, and are among the most successful catalysts. Salen ligand framework is a platform of choice thanks to its facile synthesis and modifications. In addition, aluminum is the most abundant of all metals in the earth's crust, a cheap metal with low toxicity.

Recently, bimetallic complexes have attracted great attention as they have different catalytic behaviours in comparison to their related monometallic derivatives because of the presence of two proximal reactive centres within the same complex that can act in a concerted mode. On the other hand, the use of dianionic "ONNO" type ligands as binucleating ligands for the formation of bimetallic species is definitively less explored.

The aim of the thesis is to develop simple and efficient bimetallic salen-type aluminum catalysts for the ROP of cyclic esters, as well as for the ROCOP between epoxides/anhydrides exploring the possibility of a synergistic effect when two reactive metal centres are in proximal positions.

Since the distance between the metal centres is a critical parameter to have cooperation between them, dinuclear aluminum alkyl complexes of the general formula  $L-Al_2Me_4$ , where L are salen ligands with an alkyl backbone of different lengths between the nitrogen atoms have been prepared to investigate the possibility of cooperation between reactive centres in ring-opening polymerizations. The related tetra-coordinate hemi-salen, that is phenoxy-imine monometallic complex, was also synthesized.

The activities of these aluminum complexes have been analysed for the synthesis of polyesters via both catalytic processes. A comparison of the catalytic behaviour of the bimetallic aluminum complexes and of the related monometallic complex was performed to verify the hypothesis of bimetallic mechanism.

Firstly, all complexes were tested as initiators in the ROP of several heterocyclic substrates: lactide (LA), caprolactone ( $\epsilon$ -CL) and butyrolactone (*rac*- $\beta$ -BL), cyclohexene oxide (CHO). Copolymerizations were explored in an attempt to broaden the range of the polymers of controlled microstructure produced. All complexes were subsequently used in the ROCOP of cyclohexene oxide and limonene oxide (LO) with anhydrides. The reaction conditions and in particular the optimal choice of co-catalyst, were studied. The possibility of terpolymerization for the preparation of block polyesters by combining ROP and ROCOP processes was investigated. Finally, the catalyst structure-performances relationship was further examined in the ROCOP. With the activity, an additional key parameter for a

ROCOP catalyst is the selectivity. We worked on the ligand design to obtain efficient and rigorously selective catalytic system, leading to the design of a bifunctional catalyst.