UNIVERSITÀ DEGLI STUDI DI SALERNO

DIPARTIMENTO DI CHIMICA E BIOLOGIA
DOTTORATO DI RICERCA IN CHIMICA

X CICLO (Nuova serie)

NEW CATALYSTS FOR RING-OPENING POLYMERIZATION OF CYCLIC ESTERS

Ilaria D'Auria

TUTOR
Prof. Claudio Pellecchia

CO-TUTOR
Dott.^{ssa} Mina Mazzeo

COORDINATORE
Prof. Gaetano Guerra

ABSTRACT

The Ring-Opening Polymerization of cyclic esters by metal complexes *via* coordination-insertion mechanism represents the most effective and versatile method for preparing aliphatic polyesters with a good control in terms of molecular weight, composition, microstructure and stereoselectivity.

Among the large variety of species investigated, the heteroleptic metal complexes of type [LMX], in which L is an ancillary ligand and X a nucleophilic group, have been shown to be especially interesting for their high catalytic efficiency and good control.

In the development of new and efficient catalytic systems a careful ligand design and an opportune choice of the metal are crucial features.

Ideally, the presence of sterically demanding ancillary ligands could tune the electronic and steric properties of the metal center, modulate its Lewis acidity, minimize the aggregation processes and limit deleterious transesterification reactions to enhance the catalytic activity and the degree of control on polymerization process**.**

Chelation, that is, the binding of a ligand to a metal through two or more bonds, is an efficient approach to realize this.

As previously discussed, several classes of chelating ligands have been explored as ancillary ligands for stabilizing reactive metal centers of the catalytic active species.

In this context the pincer-type ligands represent an valid alternative because of their unusual abilities in the stabilization of the metal center in coordination complexes.

Typically, the so-called pincer ligands of general formula ECE comprise an o-phenylene-derived backbone and a potentially E, C, E terdentate coordinating, monoanionic array, where E is a neutral two-electron donor such as NR_2, PR_2, OR_2, while C represents the anionic donor such as a arylic carbon or amido group.

Metal complexation with pincer ligands usually occurs with formation of two five-membered metallacycles to afford complexes with a rigid and robust structure.

In the last two decades pincer ligands have been synthesized with a wide range of donor atoms and the related pincer-metal complexes have been used in a variety of applications, in particular in catalytic chemistry.

On the contrary the examples of pincer based-metal complexes as initiators in the ring-opening polymerization of cyclic esters are completely unexplored.

In this work of thesis I describe the use of new phosphido pincer-type ligands, recently reported in literature, as ancillary ligands for the synthesis of new metal complexes as catalysts for the ring opening polymerization of the cyclic esters.

This type of ligands represents an original coordination environment in which an unusual phosphido anionic donor is flanked by phosphine neutral donors. A considerable coordinative flexibility is predictable for them because the phosphido moiety is an electronically flexible donor, as it can serve as an efficient σ and possibly π donor.

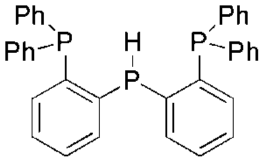
Moreover, the electronic and steric characteristic of the ligands can be finely modulated by introducing different substituent groups on the neutral phosphorous atoms .

In this work, two different diarylphosphido- disubstituted-phosphine ligands have been examinated:

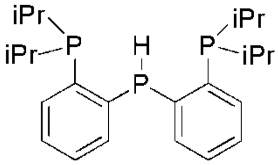
[Ph-PPP-H] bis(2-diphenylphosphinophenyl)phosphine ligand and

[iPr-PPP-H], bis(2-di-isopropylphosphinophenyl)phosphine ligand

(see figure below).



[Ph-PPP-H]



[iPr-PPP-H]

The role of the this innovative coordination environment on stability of the reactivity of different metal catalysts for the ring opening polymerization of several cyclic esters has been explored.

In general, the key parameters for the choice of metal are the polymerization control, rate and stereocontrol; further desirable features are low cost, tolerance abundance and low toxicity.

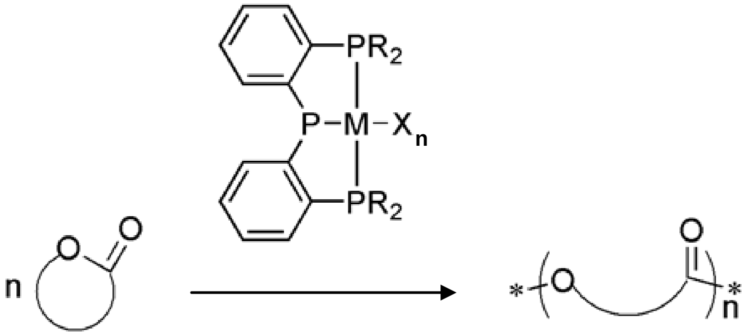
Among all metals exploited, rare-earth metal-based compounds are the most significant examples as they are very efficient catalysts for ROP of lactones due to their moderate acidity. Moreover, these compounds do not have any known toxicity.

Traditionally, zinc-based and aluminum-based complexes are also attractive initiators because they combine a very good ability in control of the polymerization reactions with relatively absence or low toxicity.

In literature examples of these metal complexes with ligands based on the hard donor elements, such as oxygen or/and nitrogen, have been largely investigated.

Differently, the use of soft donors-based ligands is rather uncommon.

In this work of thesis the synthesis of new yttrium, scandium, zinc and aluminum complexes with pincer ligands has been reported and their ability as initiators in the ring-opening polymerization of cyclic esters has been studied.



M = Y, Sc, Zn, Al

R = Ph, iPr

X = alkyl, amido, $-CH_2SiMe_3$