Abstract

The environmental and economic problems related to the petrochemical-derived polymers have driven the academic research toward the development of green and degradable alternatives to conventional plastics. The aliphatic polyesters can be considered a sustainable alternative to conventional polymer of petrochemical origin. The ring opening polymerization (*ROP*) of cyclic esters catalyzed by metal complexes allows obtaining aliphatic polyesters with controlled molecular masses using mild reaction conditions and avoids the formation of small molecule byproducts.¹ In my PhD project I focused on developing new catalytic systems for the *ROP* of cyclic esters based on group *IV* or *Al* metal complexes. The chosen metals are nontoxic, biocompatible and non-expensive, characteristics much sought after in the academic, industrial and medical fields.²

In particular in this project I developed new catalysts in which the metal is supported by linear bidentate, tetradentate and tridentate ligands that exhibit amide functions coupled with thioether groups (*NS*, *NSSN* and *NSO*). I have focused my attention on this type of ligands because amide donor ligands have been proven to be well-suite ligands for early transition metals. It is worth to note that the efficiency of group *IV* and *Al* complexes with amide ligands

in the *ROP* of cyclic esters was barely explored.³

Synthetized ligands and complexes were characterized by Mass and NMR spectroscopy, and when possible, by X-ray diffraction analysis. The catalytic performances of the complexes in the *ROP* of cyclic esters, such as L-Lactide, were extensively investigated and all, both those of group *IV* and *Al*, have been shown to be active

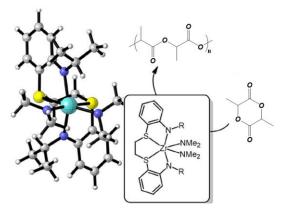


Figure 1: complex example of this project

in the polymerization. The obtained polyesters were characterized by NMR spectroscopy, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).

¹ S. M. Guillaume, E. Kirillov, Y. Sarazin, J.-F. Carpentier, *Chem. – Eur. J.*, **2015**, 21, 7988-8003; S. Kubowicz, A. M. Booth, *Environ. Sci. Technol.*, **2017**, 51, 12058-12060.

² O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.*, **2004**, 104, 6147-6176; Z. Liu, W. Gao, J. Zhang, D. Cui, Q. Wu, Y. Mu, *Organometallics*, **2010**, 29, 5783-5790; J. -C. Buffet, A. N. Martin, M. Kol, J. Okuda, *Polym. Chem.*, **2011**, 2, 2378-2384; J. -C Buffet, J. Okuda, *Chem. Commun.*, **2011**, 47, 4796-4798; A. Stopper, K. Press, J. Okuda, I. Goldberg, M. Kol, *Inorg. Chem.*, **2014**, 53, 9140-9150.

³ H. –T. Tseng, F. –S. Chen, M. Y. Chiang, W. –Y. Lu, Y. –H. Chen, Y. –C. Lai, H. –Y. Chen, *RSC Adv.*, **2015**, 5, 90682–90690; Y. Wei, S. Wang, S. Zhou, *Dalton Trans.*, **2016**, 45, 4471-4485; A. Otero, J. Fernández-Baeza, A. Garcés, L. F. Sánchez-Barba, A. Lara-Sánchez, J. Martinez-Ferrer, *Dalton Trans.*, **2017**, 46, 6654-6662.