

# “Development of new catalytic system of the group 4 metals for the polymerization of olefins and polar monomers”

## ABSTRACT

In this PhD work, a series of eight new group 4 metal complexes **1–8** (**1** = (t-BuOS)<sub>2</sub>TiCl<sub>2</sub>; **2** = (CumOS)<sub>2</sub>TiCl<sub>2</sub>; **3** = (t-BuOS)<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub>; **4** = (CumOS)<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub>; **5** = (t-BuOS)<sub>2</sub>Ti(OiPr)<sub>2</sub>; **6** = (t-BuOS)<sub>2</sub>Zr(OtBu)<sub>2</sub>; **7** = (t-BuOS)<sub>2</sub>Hf(OtBu)<sub>2</sub>; **8** = (CumOS)<sub>2</sub>Zr(OtBu)<sub>2</sub>) supported by two phenolate bidentate ligands (t-BuOS–H = 4,6-di-tertbutyl- 2-phenylsulfanylphenol and CumOS–H = 4,6-dicumyl-2- phenylsulfanylphenol) were synthesized by the reaction of appropriate metal precursors with 2 equiv of the ligands. These complexes were characterized by means of <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy and the complex **6** by X-ray diffraction.

The X-ray structure of complex **6** revealed that the two ligands were κ<sup>2</sup>-chelated to the metal center with two phenoxy groups in trans position and the two thioether moieties in *cis* position.

All these complexes exhibit fluxional behavior in solution and this was revealed by VT <sup>1</sup>H-NMR and supported by density functional theory (DFT) calculations. All these complexes are active catalysts in ethylene polymerization, producing linear polyethylene. Notably, the zirconium complex **3** displays, under proper reaction conditions, very high activity (1422 kgPE molcat<sup>-1</sup> bar<sup>-1</sup> h<sup>-1</sup>), which compares well with that of the most active post-metallocene catalysts. Furthermore, propylene polymerization catalyzed by the titanium complex **1** yields atactic polypropylene, whereas the zirconium complexes **3** and **4** selectively produce oligopropylene with Schultz–Flory distribution. NMR analysis of the unsaturated chain ends in the latter samples provides evidence of a regioselective propagation reaction with a large preference for 1,2-monomer insertion.

These complexes have also been tested in the ring-opening polymerization (ROP) of lactide and ε caprolactone. Complex **8** exhibited the highest activity with a pseudo-first-order rate constant of 0.061 ± 0.003 min<sup>-1</sup> at 100 °C, which

compares favorably with those reported for the most active group 4 complexes. Polymerizations were well-controlled, giving predictable molecular weights and narrow molecular weight distributions. In particular, atactic PLA was obtained in the ROP of *rac*-lactide. In presence of isopropanol, lower PDI indexes and molecular weights of the PLAs proportional to the equivalents of isopropanol suggested that adequate conditions for effective “immortal” polymerizations were achieved. More interestingly, these catalysts promoted the copolymerization of L-lactide and  $\epsilon$ -caprolactone. The microstructure disclosed by  $^{13}\text{C}$ -NMR analysis and the thermal behavior exhibited in DSC studies indicated a random distribution of the two monomers along the polymer chain.

Copolymers with high  $\epsilon$ -caprolactone content showed a large scale formation of crystalline spherulites prone to perfection of the crystallinity upon thermal annealing at 50 °C. Differently, L-lactide rich copolymers revealed a thin film morphology consisting of small rigid domains of L-lactide segments of about 15 nm embedded in a soft matrix of the counterpart. Copolymers with comparable mole fractions of the two monomers were entirely amorphous.

Moreover, the zirconium complex **6** was effective in the copolymerization of *rac*-butyrolactone with *rac*-lactide. The  $^{13}\text{C}$ -NMR analysis revealed that the obtained copolymers have a di-block microstructure consisting of an initial block composed of lactide sequences and an terminal block composed of butyrolactone sequences.