

Abstract and Keywords

Polyolefins constitute the largest and most commercially significant class of polymers worldwide, owing to their exceptional versatility and unparalleled range of applications in packaging, automotive, construction and consumer goods industries. Transition metal-catalyzed olefin polymerization, driven by advances from Ziegler-Natta to single-site metallocene and post-metallocene systems, has enabled precise control over polymer microstructure and properties. Systematic ligand and catalyst design, including *ansa*-metallocenes, half-metallocene, non-metallocene frameworks and emerging bimetallic systems, allows fine tuning of steric and electronic environments, leading to enhanced activity, selectivity and access to advanced polyolefin materials. Motivated by recent developments reported in the literature, we have synthesized a series of ligands for metallocene and post-metallocene titanium and zirconium complexes to investigate olefin polymerization behavior on borate activation. Firstly, a series of substituted ethylene-bridged fluorenyl-cyclopentadienyl ligands were synthesized via an efficient route that resolves the key limitations of traditional synthetic approaches. Their corresponding *ansa*-zirconocene(IV) complexes were further evaluated for ethylene homo-polymerization and ethylene/1-hexene copolymerization. Polymerization studies revealed that the substitution at the bridging carbon strongly influenced catalytic activity, molecular weight and comonomer incorporation, demonstrating that steric modulation enables effective control over polymer microstructure and catalytic performance. Furthermore, fluorene amine-based phenoxyimine Ti(IV) and Zr(IV) complexes were synthesized and systematically evaluated for ethylene homo- and copolymerization, demonstrating the profound impact of ligand modification on catalytic performance and polymer properties. Notably, the unexpected formation of a bifluorene-bridged phenoxyimine framework introduced a new structural motif, that expands the structural diversity of FI-type catalyst systems, offering promising opportunities for new catalyst development. Moreover, a synthetic route was developed to access a new class of phenoxyimine (FI)-based half-metallocene Ti(IV) and Zr(IV) systems that integrate a fluorenyl-based carbon-bridged framework with O,N-donor coordination, combining the rigidity of *ansa*-metallocenes with the modularity of post-metallocene systems. The borate activated half-metallocene catalysts were found to be

efficient for the synthesis of ultra-high molecular weight polyethylene (UHMWPE). Driven by literature precedents on bimetallic cooperativity, a carbazole-bridged di-cyclopentadienyl ligand was synthesized and employed in the preparation of Ti(IV) and Zr(IV)-based bimetallic metallocene olefin polymerization catalysts. Comparative evaluation against monometallic analogues provided insight into the advantage of metal-metal cooperativity in improving catalytic activity and polymer properties. Overall, the catalyst designing and the synthetic strategies, together with insights into structure-activity relationships, demonstrated in this doctoral thesis will certainly help in the development of next-generation polyolefin catalysts for large-scale polyolefin production with application-specific attributes.

Keywords: Ligand design, Fluorene, Carbazole, Phenoxy-imine, Organometallic complexes, Group IV metal complexes, Titanium, Zirconium, Single-site catalysts, *Ansa*-metallocene, Half-metallocene, Post-metallocene, Bimetallic catalyst, Borate activation, Olefin Polymerization, Ethylene/ α -olefin copolymerization, Polyethylene, LLDPE, Structure-activity relationship, Polymer microstructure, Thermal analysis.