

Review

Bis(pyrrolide-imine) Ti complexes with MAO: A new family of high performance catalysts for olefin polymerization [☆]

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Abstract

This contribution reports on the syntheses, structures and olefin polymerization behavior of Ti complexes having a pair of chelating pyrrolide-imine [N⁻,N] ligands. X-ray analyses as well as ¹H NMR studies demonstrate that bis(pyrrolide-imine) Ti complexes (named PI Catalysts) contain approximately octahedrally coordinated metal centers with mutually *trans*-pyrrolide-Ns, *cis*-imine-Ns and *cis*-Cls. DFT studies suggest that PI Catalysts, when activated, provide a metal alkyl in the *cis* position to a vacant coordination site for monomer binding. These theoretical studies also show that the active species derived from PI Catalysts normally possess higher electrophilicity and a sterically more open nature compared with those produced using bis(phenoxy-imine) Ti complexes (Ti-FI Catalysts) which are known as high performance olefin polymerization catalysts. These structural as well as electronic features suggest that PI Catalysts have high potential for the polymerization of olefinic monomers.

Unlike high performance Ti-FI Catalysts, PI Catalysts do not require the presence of steric bulk in close proximity to the anionic donor. PI Catalysts combined with MAO display high ethylene polymerization activities (max. 33,200 kg-polymer/mol-cat/h, 25 °C, atmospheric pressure) comparable to those obtained with early group 4 metallocene catalysts (e.g., Cp₂TiCl₂ 16,700 kg-polymer/mol-cat/h) under identical conditions. As expected, PI Catalysts exhibit higher incorporation capability for propylene and 1-hexene relative to FI Catalysts though the incorporation levels are lower than those for Cp₂TiCl₂. To our surprise, PI Catalysts/MAO show remarkably high norbornene (NB) incorporation, superior to that seen with the [Me₂Si(Me₄Cp)*N*-*t*Bu]TiCl₂ (CGC) catalyst system, and they readily form ethylene-NB copolymers with high NB contents. The highly electrophilic and sterically open nature is probably responsible for the high NB affinity. Additionally, PI Catalysts/MAO possess characteristics of living ethylene polymerization (though under limited conditions) and afford high molecular weight PEs with very narrow molecular weight distributions (M_n 225,000, M_w/M_n 1.15, 10-s polymerization, 25 °C). Moreover, these catalysts can copolymerize ethylene and NB in a highly controlled living manner to afford monodisperse alternating copolymers with very high molecular weights ($M_n > 500,000$, $M_w/M_n < 1.2$) at room temperature. This unique living nature allows the preparation of a number of ethylene- and NB-based block copolymers, including PE-*b*-poly(ethylene-*co*-NB) and poly(ethylene-*co*-NB)_{*a*}-*b*-poly(ethylene-*co*-NB)_{*b*}, in which each segment contains a different NB content. These are probably the first examples of the syntheses of block copolymers from ethylene and NB. Consequently, the discovery and application of PI Catalysts has exercised a significant influence on olefin polymerization catalysis and polymer synthesis.

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1. Introduction

A tremendous amount of academic and industrial research during the last two decades has focused on the development of highly active molecular catalysts for the controlled polymerization of olefinic monomers. Molecular catalysts typically possess well-defined, homogeneous active sites, unlike the multi-sited heterogeneous Ziegler–Natta catalysts [1]. Therefore, molecular catalysts offer the advantages of control over chain transfer reactions, comonomer incorporation and polymer stereochemistry, allowing access to a variety of polyolefinic materials with specific microstructures and narrower molecular weight distributions.

Great advances in the design and synthesis of well-defined transition metal complexes for olefin polymerization, in collaboration with the discovery of highly efficient cocatalysts, have played a salient role in activating and accelerating research aimed at developing high-activity molecular catalysts. Group 4 metallocene catalysts and constrained-geometry catalysts (CGCs) have been at the forefront of this development, creating new opportunities for producing a wide array of polymers with distinctive microstructures and enhanced performance qualities [e.g., linear low-density polyethylenes (LLDPEs), elastomers, plastomers, isotactic and syndiotactic polypropylenes (iPPs and sPPs), and syndiotactic polystyrenes (sPPSs)] [1]. In recent years, these catalysts have enjoyed success in the commercial production of differentiated polymers such as those listed above.

Due to the demand for greater control over polymer microstructures, as well as the creation of polymers with new compositions and molecular architectures, numerous attempts have been undertaken recently to develop new molecular catalysts other than the existing group 4 metallocene catalysts and CGCs. These research efforts have led to the introduction of quite a few new molecular catalysts based on both early and late transition metals with various ligand frameworks [2]. Upon activation with suitable cocatalysts, these new transition metal complexes can form highly active catalysts that create polymers with unique molecular structures, many of which were previously unobtainable with conventional catalysts (e.g., hyper-branched PEs, ethylene-polar monomer copolymers, high molecular weight monodisperse poly(1-hexene)s and polyolefinic block copolymers) [2].

Since the middle of the 1990s, our interests have centered on the discovery and application of highly active molecular catalysts based on the combination of transition metals and non-symmetric bidentate and tridentate ligands with electronically flexible properties (“ligand-oriented catalyst design research”) [3]. In connection with these studies, we discovered a number of families of transition metal complexes featuring monoanionic non-symmetric chelate ligands for olefin polymerization. These complexes, in combination with appropriate cocatalysts [e.g., MAO, $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, MgCl_2 , hetero poly compounds, clay minerals], form high-activity catalysts for the polymerization of ethylene [3a,c,d,4a–4d]. Attractive features of these molecular catalysts include

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