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VIP Polymerization Catalysts

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Salalen Titanium Complexes in the Highly Isospecific Polymerization of 1-Hexene and Propylene**

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Dedicated to Professor Adolfo Zambelli on the occasion of his 77th birthday

Isotactic polypropylene (*i*PP) is a thermoplastic material of vast importance. The ever-increasing demand for it is derived from its useful physical properties and the availability of its feedstock, propylene. The most important microstructural property of polypropylene is the degree of isotacticity, which, combined with sufficiently high molecular weight, determines its melting point (T_m) and thereby its possible applications.[1] *i*PP produced by heterogeneous Ziegler–Natta catalysts has typical T_m values not exceeding 165 °C.[2–5] Homogeneous catalysts of the metallocene,[6] and, more recently, nonmetallocene[7] families lead to polymers possessing narrower molecular weight distributions. However, in spite of considerable research efforts in the last 25 years, only a few such systems were found to lead to *i*PP having T_m values approaching those obtained by the heterogeneous catalysts.[8,9] Herein, we describe a family of nonmetallocene catalysts for olefin polymerization based on a new design concept. Certain members of this family led to polypropylene of exceptionally high isotacticities and T_m values.

Isospecific catalysts are capable of discriminating between the two enantiotopic faces of an incoming olefin. This differentiation is achieved through the different interactions of these faces with the preferred conformation of the bound polymeryl chain, which is oriented by its interactions with substituents in the vicinity of the chiral metal environment. C_2-symmetric catalysts are relatively accessible, and their two coordination sites are homotopic, so their induction of isospecificity is independent of possible epimerization events of the polymeryl chain. C_1-symmetric complexes are structurally more diverse, but the directing abilities of their two diastereotopic sites are usually different. So, a successful design of highly isospecific C_1-symmetric catalysts should include a directional polymeryl chain migration to the more selective site.[10] This approach was previously developed for C_1-symmetric metallocenes bearing an overly crowded site from which the polymeryl chain skips into the less crowded and more directing site,[11,8d] as visualized in the appropriate quadrant representation (Figure 1, left).[12] In designing the current catalysts, we envisioned that a directional site epimerization might also be promoted electronically, namely, by placing donors of different *trans* influence *trans* to the two coordination sites in an octahedral environment (Figure 1, right).

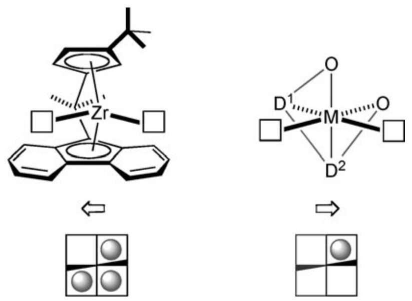

Figure 1. Induction of directional polymeryl site epimerization by steric pressure in C_1-symmetric metallocenes (left) and electronic *trans* influence in octahedral *fac–mer* complexes of tetradentate {OD^{1}D^{2}O}-type ligands (right; D = donor). The bottom drawings are the corresponding quadrant representations.

The tetradentate {ONNO}-type salan ligands tend to wrap around Group 4 metals in the symmetric *fac–fac* mode, giving octahedral complexes of the type [{ONNO}MX$_2$] (X = O-*i*Pr, benzyl (Bn), etc.).[13] The ability of the dibenzyl complexes to promote isospecific polymerization in the presence of cocatalysts such as $B(C_6F_5)_3$ or methylalumoxane (MAO) depends on the steric bulk of the phenolate substituents and on the metal.[14] Recently, we showed that C_1-symmetric zirconium complexes derived from nonsymmetrically substituted salan ligands led to averaging of tacticities, thus implying that a random polymeryl site epimerization was taking place.[15] To promote a directional site epimerization, a tetradentate ligand wrapping in a nonsymmetric manner would be required. Thus, we turned to the salalens. Salalens are half-salan/half-salen hybrid ligands, found to preferably wrap around octahedral Group 4 metal centers so that the half-salan O,N,N donors bind in a *fac* mode and the half-salen O,N,N donors bind in a *mer* mode.[16] This *fac–mer* wrapping places one coordination site *trans* to the neutral imine N donor and the other site *trans* to the anionic phenoxy O donor, thus satisfying the above requirement.[17] Complexes

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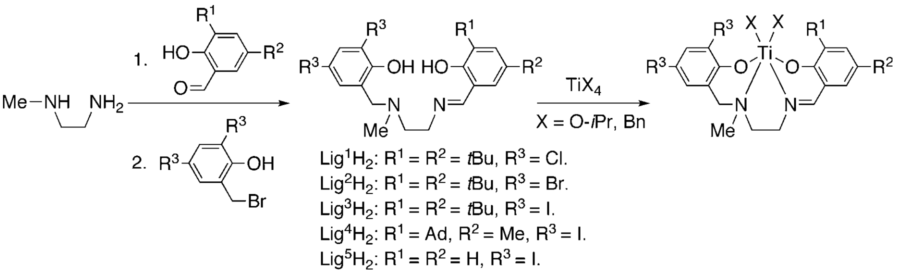
of salalen ligands were reported to catalyze various transformations, including asymmetric oxidations[18] and epoxide–CO_2 polymerization,[19] but to date they have not been employed in olefin polymerization catalysis.



Scheme 1. Synthesis of salalen ligands and complexes.

Five salalen ligand precursors were screened initially ($Lig^{1-5}H_2$, Scheme 1). They were designed to include alkyl groups of different sizes (H, *tert*-butyl, adamantyl) on the phenolate ring close to the imine donor and halides of different sizes (Cl, Br, I) on the phenolate ring close to the amine donor to enable the evaluation of their individual effects. The ligand precursors were all synthesized by a two-step reaction sequence consisting of condensation of the primary amine of *N*-methyldiaminoethane with a substituted salicylaldehyde and subsequent nucleophilic attack of the secondary amine on the bromomethyl derivative of the corresponding phenol (see the Supporting Information). The ligand precursors reacted with tetra(isopropoxide)titanium and with tetrabenzyltitanium to give mononuclear complexes of the types $[Lig^{1-5}Ti(O\text{-}i\text{Pr})_2]$ and $[Lig^{1-5}TiBn_2]$, respectively, as single diastereomers of C_1 symmetry.

We propose that the salalen ligands wrap diastereospecifically in the *fac–mer* mode in all complexes. Single crystals of $[Lig^4Ti(O\text{-}i\text{Pr})_2]$ were grown from cold toluene. Single-crystal X-ray crystallographic analysis revealed the expected mononuclear *fac–mer* complex. The difference in quadrant occupancy between this complex and the seemingly related complex of the salan ligand that features the same phenolate rings but wraps in a *fac–fac* mode is clearly apparent (Figure 2).[20] The bond lengths of $[Lig^4Ti(O\text{-}i\text{Pr})_2]$ were typical of the salan and salen structural motifs. A slightly longer bond for the isopropoxo group *trans* to the phenoxy group (1.825(2) Å) relative to that *trans* to the imine donor (1.807(2) Å) may indicate the former's weaker bonding.

The three complexes of the salalen ligands with *tert*-butyl-substituted phenolates ($[Lig^{1-3}TiBn_2]$) exhibited mild activities in neat 1-hexene polymerization after activation with $B(C_6F_5)_3$ (4.5–18 $g\,mmol^{-1}\,h^{-1}$ for polymerization reactions of 2–4 h). Very narrow molecular weight distributions (with polydispersity indices (PDIs) as low as 1.04) supported the living nature of the polymerizations. However, the very high polymer molecular weights ($M_n = 360\,000–390\,000$) relative to the calculated values ($M_{calcd} = 9300–48\,000$; obtained by dividing the amount of polymer obtained by mole of precatalyst employed) indicate partial precatalyst activation under these conditions. ^{13}C NMR spectroscopy revealed that the degree of isotacticity in these polymers depended on the size of the halide substituent, with $[mmmm] = 63\,\%$ (Cl), 79 % (Br), and 94 % (I). Replacing the *t*Bu substituent in Lig^3 with either a larger substituent (Ad, Lig^4) or a much smaller substituent (H, Lig^5) had little effect on the isotacticity of the resulting poly(1-hexene) ($[mmmm] = 89\,\%$ and 87 %, respectively). In other words, only the substituents of the phenolate proximal to the amine donor play a significant stereodirecting role under these conditions. In comparison, for C_1-symmetric salan ligands that wrap in the *fac–fac* mode, the substituents on both rings affect the isotacticity of the resulting poly(1-hexene).[15]

The salalen complexes $[Lig^{1-5}TiBn_2]$ were found to be suitable for polymerization of liquid propylene (cryogenically condensed in a stainless steel reactor, thawed, and let stir for 14 h at 25 °C; see the Supporting Information) with 500 equivalents of MAO as cocatalyst. All the polymer samples were obtained as crystalline solids. The complexes containing the *tert*-butyl-substituted phenolates ($[Lig^{1-3}TiBn_2]$) yielded highly isotactic polypropylene with $[mmmm] = 90$, 96, and 96 % according to ^{13}C NMR spectroscopy and melting points of 150, 157, and 155 °C. A 2:2:1 ratio of the $[mmmr]$, $[mmrr]$, and $[mrrm]$ pentad peaks for those samples was consistent with enantiomorphic site control of stereoregularity.[21] No regioerror or chain-end peaks could be detected in those spectra. The complex $[Lig^4TiBn_2]$, featuring the bulky adamantyl group, yielded polypropylene of $[mmmm] \geq 99\,\%$ and a melting transition of 164 °C, which is one of the highest ever reported for a homogeneous titanium catalyst.[8b,22] The stereoerrors are hardly observable for this polymer, but they are also consistent with an enantiomorphic site-control mechanism. In contrast, the sterically unhindered complex $[Lig^5TiBn_2]$ gave rise to mostly stereoirregular polypropylene, as evident from its very low degree of

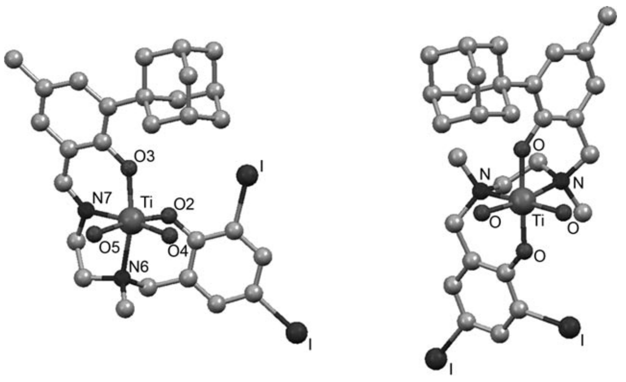
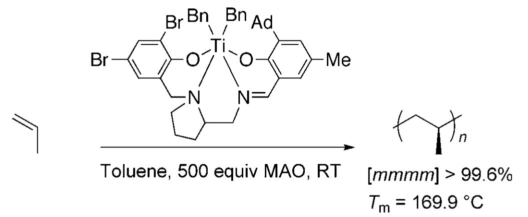


Figure 2. Left: Crystal structure of *fac–mer* $[Lig^4Ti(O\text{-}i\text{Pr})_2]$ with *i*Pr groups omitted for clarity. Selected bond lengths [Å]: Ti–O2 2.003(2), Ti–O3 1.889(2), Ti–N6 2.325(3), Ti–N7 2.194(2), Ti–O4 1.807(2), Ti–O5 1.825(2). Right: Crystal structure of the corresponding *fac–fac* $[\{salan\}Ti(O\text{-}i\text{Pr})_2]$ complex.

crystallinity and its ^{13}C NMR spectrum. All polymers had high molecular weights and narrow molecular weight distributions, as expected for homogeneous systems.

Notably, the ligand substituents have different effects on stereospecificities in polymerization of the two monomers, evident in particular for the adamantyl group. Most unusually, the higher isotacticities of polypropylene relative to poly(1-hexene) are opposite to the common trend of substantially lower stereocontrol for the "slimmer" olefin.[14c] To test whether the change of cocatalyst was responsible for this opposite trend, we repeated the polymerizations of 1-hexene with [Lig$^{1-5}$TiBn$_2$], this time employing 500 equivalents of MAO as cocatalyst. Very high activities of up to 11 700 g mmol^{-1} h^{-1} were found (boiling of the monomer within a few seconds after the addition of MAO to the neat monomer was observed), and, except for [Lig^{5}TiBn$_2$], all precatalysts led to poly(1-hexene) of higher isotacticities ([*mmmm*] = 76–96 %) relative to those obtained with B(C$_6$F$_5$)$_3$ as cocatalyst. We found that as little as 50 equivalents of MAO were sufficient to produce highly active catalysts (For [Lig^{4}TiBn$_2$]: 600 g mmol^{-1} h^{-1}; [*mmmm*] > 99 %). The narrow molecular weight distributions and high molecular weights testify to the single-site nature of the catalysts and the negligible chain transfer to MAO. We presume that the enhancement of isospecificity (and activity) by employing MAO rather than B(C$_6$F$_5$)$_3$ as cocatalyst results from different catalyst–counteranion interactions,[23] which have been proposed to affect site epimerization rates.[24,25]

We found that polypropylene of even higher isotacticities could be obtained by assembling the salalen ligands around the chiral rigid aminomethylpyrrolidine backbone. For example, Lig^{6}H$_2$, a salalen ligand precursor featuring the bulky adamantylphenolate on the imine side arm and a dibromophenolate on the amine side arm, led to [Lig^{6}TiBn$_2$] as a single diastereomer (Scheme 2). Polymerization of liquid propylene yielded crystalline polypropylene with an extremely high degree of stereoregularity ([*mmmm*] = 99.6 %) and an even higher degree of regioregularity (no observable peaks between $\delta = 30$ and 45 ppm), as apparent from its ^{13}C NMR spectrum (Figure 3). Correspondingly, it exhibited a very high T_m of 168.3 °C. For polymerization in toluene solution (33.5 psig$_{\text{propylene}}$, 500 equiv MAO, RT), this catalyst exhibited a very high activity exceeding 10 000 g mmol^{-1} h^{-1}, and the isotactic polypropylene formed had a T_m of 169.9 °C. To our knowledge, this is the highest melting transition reported for "as prepared" (not extracted or annealed) isotactic polypropylene produced by either heterogeneous or homogeneous catalysts and measured by a standard differential scanning calorimetry (DSC) protocol (see the Supporting Information).[5] It implies that the polypropylene obtained is of the highest degrees of regio- and stereoregularity reported to date.



Scheme 2. Structure and catalytic performance of [Lig^{6}TiBn$_2$].

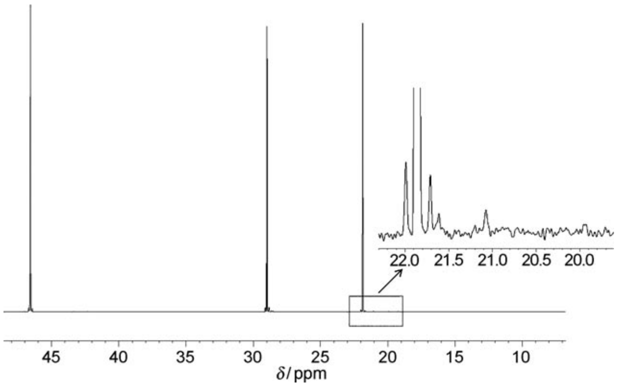


Figure 3. ^{13}C NMR spectrum (C$_6$D$_4$Cl$_2$) of polypropylene prepared with [Lig^{6}TiBn$_2$]/neat propylene/MAO. Inset: Expansion of the methyl region. The peaks in the vicinity of the *mmmm* peak are the ^{13}C satellites. [*mmmm*] = 99.6 %.

In conclusion, we have introduced a new family of octahedral C_1-symmetric titanium catalysts for isospecific polymerization, relying on the readily available and structurally diverse salalen ligands. The ability to control the degree of isotacticity, and, in particular, the synthesis of polypropylene samples with extraordinarily high isotacticities and melting transitions indicates that the wealth of structural motifs in nonmetallocenes is far from exhausted. Such catalysts are expected to produce polymeric materials not accessible with more traditional catalysts. Mechanistic studies aimed at revealing the involvement of site epimerization, further catalyst development based on the concepts introduced herein, and application of these catalysts in other polymerizations are underway.

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