

Same Ligand, Different Metals: Diiodo–Salan Complexes of the Group 4 Triad in Isospecific Polymerization of 1-Hexene and Propylene

Ad Cohen,[†] Jacob Kopilov,[†] Marina Lamberti,[‡] Vincenzo Venditto,[‡] and Moshe Kol^{*,†}

[†]School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel, and [‡]Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, I-84084 Fisciano (SA), Italy

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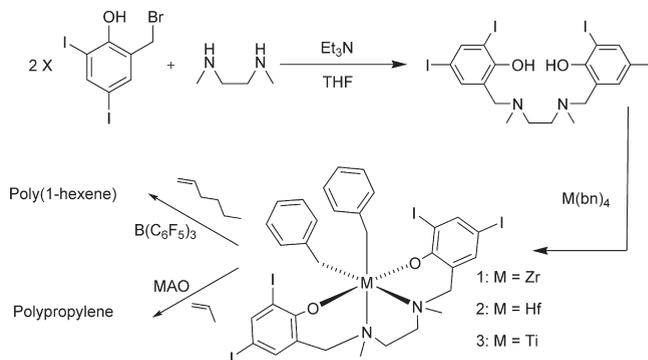
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The design of catalysts that will enable the living polymerization of propylene with high activities and isoselectivities under ambient conditions remains a challenge in current polymer chemistry.¹ Such polymerization may give rise to specialty polymers like elastomers, obtained by block copolymerization of ethylene and propylene by sequential monomer addition.^{2,3} Since metallocene catalysts do not lead to living polymerization under ambient temperatures, the search for such catalysts lies in the regime of group 4 metal non-metallocenes.⁴ In the past decade, several noteworthy systems were introduced that led to isoselective polymerization of high olefins such as 1-hexene. While the degree of the polymers isotacticity is determined by the ability of the ligand(s) bound to the metal center to direct the incoming olefin via a preferred enantioface, it is also strongly affected by the bulk of the olefin, with higher olefins commonly giving rise to more stereoregular polymers. Thus, the Salan–,⁵ the Cp*/amidinate–,⁶ and the amidomethylpyrrolidopyridine–zirconium⁷ catalysts that led to almost perfectly isotactic poly(1-hexene) gave reduced tacticities in polypropylene of [mmmm] of 79%,⁸ 71%,^{9,10} and 73%,⁷ respectively. A similar trend was reported for the binaphthyl-bridged Salen–zirconium catalyst (81→11% [mmmm]).¹¹

Zirconium–Salan complexes were found to lead to isoselective polymerization of 1-hexene only if the ligands included bulky *ortho*-substituents on the phenolate rings.⁵ Their activity was low. Replacing the bulky alkyl groups with electron-withdrawing chloro or bromo groups led to higher activities but to stereoirregular poly(1-hexene). We reasoned that binding the same ligands to a smaller metal atom, i.e., titanium, may intensify their effective bulk, leading to increased degree of isotacticity, which was indeed found, but was not high.¹² In this work we describe the synthesis of a Salan ligand featuring diiodo-phenolate rings, the dibenzyl complexes of this ligand with the group 4 triad metals, and the polymerization of 1-hexene and propylene by these complexes. The polymerization of propylene by titanium–Salan complexes was not reported previously, and the activity of such a catalyst, revealed herein, is quite remarkable.

The attempted synthesis of the target ligand precursor by the Mannich condensation¹³ between *N,N'*-dimethylethylenediamine, formaldehyde, and 2,4-diiodophenol failed. We therefore reverted to an alternative reaction¹⁴ between this diamine and the bromomethyl derivative of that phenol (obtained by borohydride reduction of diiodosalicylaldehyde followed by HBr treatment; see the Supporting Information) that gave the ligand precursor LigH₂ in 56% yield. LigH₂ reacted with the tetrabenzyl

Scheme 1. Synthesis of the Ligand, the Dibenzyl Complexes, and the Polymers Described in This Work



derivatives of the group 4 triad to give the corresponding LigMBn₂ (M = Zr, Hf, Ti) complexes as yellow, white, and brown solids, respectively, that could be stored at –30 °C as solids. The zirconium and hafnium complexes were relatively stable in toluene solution at RT, whereas the titanium complex decomposed readily. ¹H NMR characterization indicated that all complexes formed as single isomers of C₂ symmetry, signifying a *fac*–*fac* ligand wrapping and *cis* relationship between the two benzyl groups typical of Salan ligands and essential for olefin polymerization catalysis (Scheme 1).

Upon activation with tris(pentafluorophenyl)borane all complexes led to active polymerization catalysts of neat 1-hexene at RT, as apparent from the polymerization mixtures becoming viscous within a few minutes. As expected, the zirconium complex led to the most active catalyst with an activity of 3800 g mmol^{–1} h^{–1}; the hafnium and titanium complexes exhibited somewhat lower activities of ca. 1500 g mmol^{–1} h^{–1}. While the lower activity of the hafnium relative to the zirconium catalyst is in line with previous findings, the activity of the titanium catalyst is high when taking into account the instability of the dibenzyl complex LigTiBn₂ in solution. Evidently, the active cationic species is stable enough to sustain a long-lasting polymerization. GPC analysis revealed that the Zr catalyst led to a low molecular weight poly(1-hexene) of M_w = 14 000 and PDI = 2.0, signifying a nonliving single-site catalyst. The Hf and Ti catalysts led to high molecular weight polymers of 320 000 (PDI = 1.7) and 410 000 (PDI = 1.4), respectively. The molecular weight trend is consistent with the reduced termination/propagation tendencies of these metals.^{3,12} Pentad analysis by ¹³C NMR revealed that the polymer samples were isotactic to different extents (Figure 1a). The Zr catalyst led to poly(1-hexene) of [mmmm] of 33%, which is low, but higher than that obtained from the corresponding dibromo–Salan–Zr complex (atactic);¹² i.e., the increase in the size of halo substituent from bromo to iodo was sufficient to induce an apparent isotacticity.¹⁵ The Hf and Ti catalysts led to higher isotacticities of [mmmm] of 50% and 87%, respectively, as expected. Pentad overlap in the samples of lower isotacticities hampered the determination of stereochemical control mechanism. However, the presence of an isolated *mrrm* pentad as the only impurity (besides the *mmmr* and *mmrr* overlapping the *mmmm* peak)¹⁶ in the titanium derived highly isotactic polymer gives a strong support for an enantiomorphic site control mechanism. We propose that a similar mechanism operates for the zirconium and hafnium complexes.

*Corresponding author. E-mail: moshekol@post.tau.ac.il.

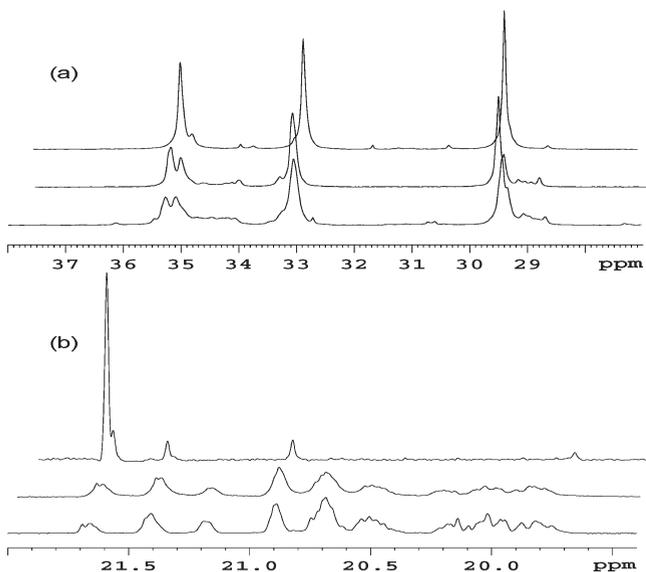


Figure 1. ^{13}C NMR spectra of carbons 3, 2, and 4 of the poly(1-hexene) samples (a) and methyl region of polypropylene samples (b) produced by Zr (bottom), Hf (middle), and Ti (top) Salan catalysts.



Figure 2. Polypropylene samples prepared by the Zr-, Hf-, and Ti-Salan catalysts (left to right).

We found that solid MAO was a suitable cocatalyst for the polymerization of propylene by these halo-containing Salan complexes, without the need for a chain transfer quencher.³ Preliminary experiments included the polymerization of neat propylene by its cryogenic condensation into a reactor containing the solid dibenzyl complex and MAO, slow thawing, and stirring at RT for 16 h. While this setup does not allow activity measurements, it is noteworthy that a considerable portion of the propylene was consumed by all catalysts. With low-to-imperfect isoselectivities in 1-hexene polymerizations, we expected these catalysts to exhibit considerably lower isoselectivities in polymerization of the smaller monomer. Indeed, the zirconium and hafnium catalysts led to practically atactic polymers having $[mmmm]$ of 6% and 10%, respectively. However, in contrast to the gradual trend observed for the 1-hexene polymerization, the titanium catalyst led to polypropylene whose isotacticity was almost the same as that of the poly(1-hexene): $[mmmm]$ of 80% ($[rr] = 4.0\%$, Figure 1b). A clear $[mmmmr]:[mmrr]:[mrrm]$ ratio of 2:2:1 indicates an enantiomorphic site control mechanism.

The molecular weights were strongly dependent on the metal employed: 4000, 37 000, and 1 050 000 for the Zr, Hf, and Ti catalysts, respectively. The physical attributes of the polymer samples were consistent with their tacticities and molecular weights: oils of medium and high viscosity and a white crystalline solid, respectively (Figure 2). ^{13}C NMR revealed that the polymer samples were highly regioregular. Chain-end analysis of the low- M_w polypropylene derived from the Zr catalyst revealed vinylidene and *n*-propyl groups as major chain ends, supporting a regular 1,2-insertion prior to a hydride-transfer termination event. Very low intensity peaks of an isobutyl end group indicate that chain transfer to aluminum is a very minor termination process.¹⁷ The ultrahigh- M_w polymer obtained with the Ti

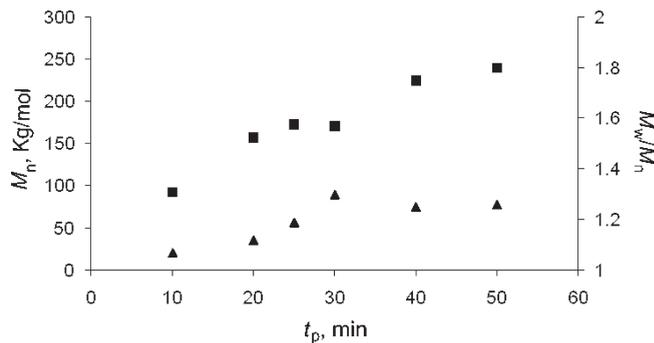


Figure 3. M_n (■) and M_w/M_n (▲) versus polymerization time for polypropylene samples obtained from LigTiBn₂ at ambient conditions (1 bar, 27 °C).

catalyst implied that chain transfer to aluminum is not an important termination mechanism for this catalyst.

Next, we attempted the polymerization of propylene under more uniform conditions, aiming to address the activity and possible living character of the titanium catalyst. The polymerization was done by passing of propylene (1 bar, $[\text{C}_3\text{H}_6] = 0.66 \text{ M}$)¹⁸ at 27 °C in toluene solution with MAO as cocatalyst. Since LigTiBn₂ is not stable in solution, we formed it *in situ* by mixing of LigH₂ and TiBn₄ in toluene under propylene atmosphere for 5 min prior to adding the MAO. Samples were taken at given intervals until the reaction mixture was observed to be heterogeneous (after 50 min). These results are represented in Figure 3. With M_n of 157 000, a very narrow PDI of 1.12, and activity of $390 \text{ g}_{\text{PP}} \text{ mmol}_{\text{CAT}}^{-1} \text{ h}^{-1} \text{ M}^{-1}$ after 20 min of polymerization, this catalyst features a rare combination of high activity and controlled character.¹⁹ A slight broadening of PDI's after this period might be due to polymer precipitation. The final molecular weight after 50 min was $M_n = 240 000$ (PDI = 1.26). These M_n and PDI values represent the most controlled polymerization of propylene by Salan complexes reported to date.³ The controlled character is unusual considering the polymerization temperature, the low monomer concentration, the lack of chain-transfer quencher, and the instability of the precatalyst in solution. The activity of this catalyst in propylene polymerization is the highest activity reported for propylene polymerization by Salan complexes.⁸ Relative to the original Salan-zirconium catalyst,^{5,8} the Salan-titanium catalyst reported herein is more than 100 times faster and leads to polypropylene of much higher molecular weight while exhibiting a slightly better isoselectivity ($[mmmm]$ of 82% was found for the polypropylene prepared at 1 bar).²⁰

Several polypropylene samples produced under various conditions (see the Supporting Information) by the titanium catalyst were analyzed by differential scanning calorimetry. They showed (second heating cycle) melting transitions in the temperatures of 120.9–123.8 °C, which are consistent with the $[mmmm]$ of 80–83%. Yet, the heat of fusion for these samples of $64.2\text{--}72.0 \text{ J g}^{-1}$ is higher than polypropylene samples of similar tacticities prepared with metallocene catalysts²¹ and possibly indicates a higher degree of crystallinity. The “as produced” samples (having $[rr]$ of ca. 3.4–4.0%) were also analyzed by X-ray powder diffraction and were found to feature very similar crystallinity and include only the α -form of the isotactic polypropylene.²² We are currently studying the effect of isothermal crystallization at different temperatures on the crystal forms of these polymers.

In conclusion, we have found that a Salan-titanium complex leads to a rare combination of activity, controlled character, and isoselectivity in propylene polymerization at RT, with the common MAO as cocatalyst. This work demonstrates that a substantial decrease in isoselectivity on going from higher α -olefin

polymerization to propylene polymerization is not a general rule, that unstable precatalysts may lead to very well-behaved polymerization catalysts, and that titanium may well be the metal of choice in Salan-based polymerization catalysis. We are currently investigating the activity of this and related catalysts in copolymerizations.

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Supporting Information Available: Experimental details for the synthesis of the ligand and complexes, polymerization details, and polymer characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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