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Oscillating Non-Metallocenes – from Stereoblock-Isotactic Polypropylene to Isotactic Polypropylene via Zirconium and Hafnium Dithiodiphenolate Catalysts

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Octahedral group 4 complexes of a new bulky tetradentate dithiodiphenolate {OSSO}-type ligand that oscillate between two enantiomeric C_2-symmetric conformations are described. The dibenzyl Zr and Hf complexes led to active catalysts in propylene polymerization. Polypropylene having predominantly stereoblock-isotactic microstructure or predominantly isotactic microstructure could be obtained by varying the polymerization conditions. Long isotactic blocks of 50 to more than 100 repeat units were formed at –10 °C in liquid propylene.

Introduction

Fluxional complexes form a rare and intriguing class of α-olefin polymerization catalysts, for which the rearrangement of spectator ligand(s) during polymer growth gives rise to two or more active conformations.[1] The relationship between these conformations (enantiomers, diastereomers, linkage isomers) and the relative rates of polymer growth and catalyst flip determine the type of polymer that is produced. If at least one of these conformations is stereodirecting, and the rate of catalyst flip is slower than that of monomer insertion, then a stereoblock copolymer may be produced from a single monomer.[2–5] The most familiar fluxional catalysts are the bis(arylindenyl) zirconocenes introduced by Waymouth in 1995.[6] They were initially proposed to oscillate between two active diastereomeric conformations: a C_2-symmetric isoselective conformation and a C_s-symmetric nonselective conformation, with the consequent formation of polypropylene having an isotactic-atactic stereoblock microstructure. Further NMR spectroscopic investigations revealed that the microstructure of the polypropylene depended on the nature of the aryl group:[7] catalysts featuring nonsubstituted aryl groups led to mixtures of polymers containing isotactic blocks separated by short stereo-irregular blocks, whereas catalysts featuring bulky aryl substituents led to polypropylene with isotactic-stereoblock microstructure consistent with interconverting catalyst enantiomers.[7,8] Herein we introduce oscillating non-metallocenes, dithiodiphenolate complexes of zirconium and hafnium, which lead to polypropylene of either predominantly stereoblock-isotactic[9] or predominantly isotactic microstructure (see Figure 1) when the ratio of insertion-to-flip rates is tuned.

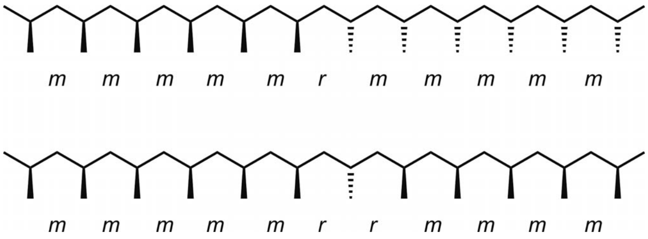

Figure 1. Top: stereoblock-isotactic polypropylene; block junctions are identified by *mmmr* and *mmrm* pentads in a 2:2 ratio. Bottom: isotactic polypropylene; isolated stereoerrors are identified by *mmmr*, *mmrr*, and *mrrm* pentads in a 2:2:1 ratio.

Recently, we described an {OSSO}-type dithiodiphenolate ligand that features a dithioethane core bridged by methylene groups to di-*tert*-butylphenol arms, and its titanium and zirconium complexes. These octahedral complexes are fluxional, exhibiting low barriers to inversion between the two C_2-symmetric *fac-fac* enantiomers.[10] The dibenzylzirconium complex led to aspecific 1-hexene polymerization following activation with tris(pentafluorophenyl)borane.[11,12] Ishii and co-workers later reported that, by constructing an analogous {OSSO} ligand around the *trans*-1,2-dithiocyclooctane core, a rigid dibenzylzirconium complex was obtained that led to isospecific 1-hexene polymerization catalysis under similar polymerization conditions ([*mmmm*] $> 95\%$).[13,14] This signifies that the stereoirregularity of the poly(1-hexene) obtained by the original {OSSO} system is due to its fluxionality rather than to insufficient monomer enantioface discrimination, which im-

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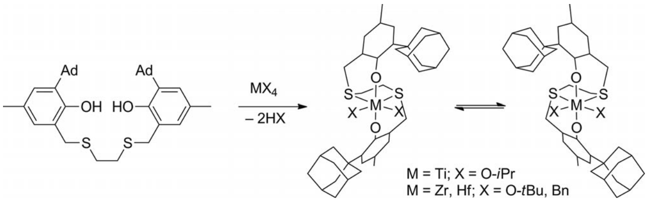
plies that fluxional {OSSO}-based catalysts that feature high enantiofacial selectivity combined with faster monomer insertion rate relative to catalyst inversion rate may lead to polymers of uncommon microstructures.

For investigating this possibility, propylene (rather than higher olefins) is the monomer of choice, because the microstructure of polypropylene is more easily deciphered from its ^{13}C NMR spectrum[15] and because its stereoregularity is reflected in its physical properties. Yet, as has been previously demonstrated for several catalytic systems, it is more challenging to distinguish between the enantiofaces of the "slim" propylene monomer relative to those of bulkier ones by given stereospecific catalysts.[16] A suitable ligand should therefore include bulky enough phenolate substituents so that its complexes would feature more distinct quadrants.[17]

Results and Discussion

The {OSSO} ligand that we targeted included bulky 1-adamantyl *ortho*-phenolate substituents (Scheme 1), because the enantiofacial discrimination ability of the 1-adamantyl substituent was found to be superior to that of the *tert*-butyl substituent for several octahedral complexes of tetradentate ligands.[18] The ligand precursor was synthesized in a single step by reacting dithioethane with the corresponding bromomethylphenol according to the previously developed methodology (see the Supporting Information).[10] Alkoxide complexes of the group 4 triad of the type [{OSSO}M(OR)$_2$] (M = Ti, R = isopropyl; M = Zr, Hf, R = *tert*-butyl) were obtained in practically quantitative yields by alcohol elimination reactions between the {OSSO}H$_2$ ligand precursor and the corresponding M(OR)$_4$ complexes. ^{1}H NMR spectra indicated that all complexes are mononuclear and fluxional.



Scheme 1. The {OSSO}H$_2$ ligand precursor and its fluxional C_2-symmetric complexes.

Variable-temperature ^{1}H NMR spectroscopic experiments in [D$_8$]toluene revealed that, for all complexes, the stable conformation was C_2-symmetric, which is consistent with *fac-fac* {OSSO}-ligand wrapping, in which the two phenoxide O-donors are mutually *trans* and the two labile alkoxide groups are mutually *cis* in a presumed octahedral environment. Different barriers to enantiomer inversion were found for the three metals: $\Delta G^‡ = 12.7 \pm 0.5$ kcal/mol for Ti; $\Delta G^‡ = 17.8 \pm 0.5$ kcal/mol for Zr; $\Delta G^‡ = 18.6 \pm 0.5$ kcal/mol for Hf (see Figures S1–S6 in the Supporting Information). The much higher barriers for inversion around the heavier metals relative to titanium may be due to stronger soft–soft interactions with the S-donors. Slightly lower barriers for inversion were previously reported for the titanium and zirconium complexes of the {OSSO} ligand featuring the less bulky *tert*-butyl substituents ($\Delta G^‡ = 11.6 \pm 0.5$ kcal/mol for Ti; $\Delta G^‡ = 17.0 \pm 0.5$ kcal/mol for Zr).[10] The dependence of inversion barriers on the bulk of phenolate substituents has been previously recorded for other systems, such as aminetris(phenolate) complexes.[19] Crystals of [{OSSO}Ti(O-*i*Pr)$_2$] and [{OSSO}Zr(O-*t*Bu)$_2$] suitable for X-ray analysis were grown at –30 °C from toluene/pentane and ether solutions, respectively, and the structures were solved to reveal the expected geometry (Figure 2).[20] As expected for a ligand that binds through long sulfur–metal dative bonds, the phenol rings are pulled towards the S-donors, bringing the adamantyl substituents close to the *cis*-related labile alkoxide groups, which point in the opposite direction to avoid steric encumbrance. Dibenzyl complexes of zirconium and hafnium of the type [{OSSO}M(Bn)$_2$] were synthesized by reacting the ligand precursor with tetrabenzylzirconium and tetrabenzylhafnium, respectively, and they appeared to be rigid C_2-symmetric mononuclear complexes at room temperature according to their ^{1}H NMR spectra. Disappointingly, well-defined dibenzyl- or dichlorotitanium complexes have not been obtained to date.

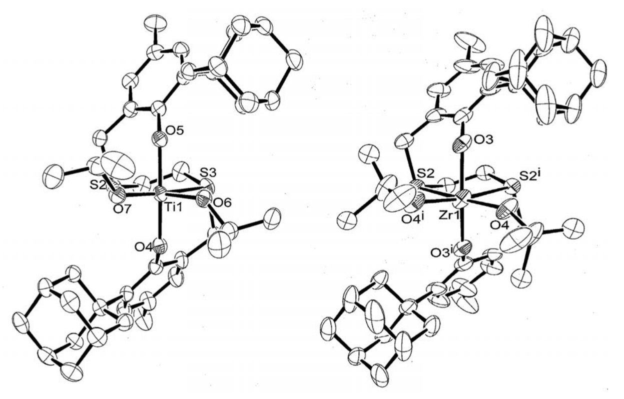


Figure 2. ORTEP representations of the crystal structures of [{OSSO}Ti(O-*i*Pr)$_2$] (left) and [{OSSO}Zr(O-*t*Bu)$_2$] (right). Selected bond lengths [Å] and angles [°] for [{OSSO}Ti(O-*i*Pr)$_2$]: Ti–S2 2.7338(8); Ti–S3 2.7040(8); Ti–O4 1.884(2); Ti–O5 1.880(2); Ti–O6 1.810(2); Ti–O7 1.816(2); S2–Ti–S3 75.53(2); O4–Ti–O5 159.76(8); O6–Ti–O7 107.03(8). For [{OSSO}Zr(O-*t*Bu)$_2$]: Zr–S2 2.828(1); Zr–O3 2.026(3); Zr–O4 1.933(3); S2–Zr–S2′ 73.84(5); O3–Zr–O3′ 152.8(2); O4–Zr–O4′ 107.1(2).

To explore the possibility of attaining polypropylene with varying microstructures by these fluxional catalysts, we employed the dibenzyl complexes [{OSSO}Zr(Bn)$_2$] and [{OSSO}Hf(Bn)$_2$] activated with 500 equiv. of MAO under different propylene pressures and polymerization temperatures. With presumed monomer-concentration-dependent insertion rate, and monomer-concentration-independent catalyst flip rate, a higher propylene concentration is expected to lead to longer blocks. Temperature may have a more intricate effect on the polymer microstructure as both the insertion and flip rates are temperature-dependent, and, in addition, monomer enantiofacial selectivity is typically temperature-dependent as well. Both catalysts exhibited moderate activities for polymerization of propylene in toluene solution at 3.2 and 1.0 bar at room temperature ([C_3H_6] = 2.15 and 0.63 M, respectively, see the Supporting Information). The polypropylene samples obtained had relatively low molecular weights and narrow molecular weight distributions, consistent with single-site catalysts. ^{13}C NMR spectra revealed an almost completely atactic polypropylene microstructure ([*mmmm*] = 9–11%). Lowering the polymerization temperature to –10 °C ([C_3H_6] = 4.5 M), led to a zirconium catalyst of low activity (the hafnium catalyst was practically inactive) and to polypropylene with low molecular weight. ^{13}C NMR spectroscopic analysis indicated that the isotacticity of the polypropylene increased, leading to a [*mmmm*] of approximately 19%. The two other major peaks in the spectrum were the *mmmr* and *mmrm* pentads of approximately 20% each. Although all pentads are observable in the ^{13}C NMR spectrum, it is noteworthy that those corresponding to the enantiomorphic site control *rr*-type error, that is, the *rrrr*, *mrrr*, and *mrrm* pentads are of considerably lower intensity than the other pentads (See Figure S8 and Table S3 in the Supporting Information). The unusually high intensity of the *mmrm* pentad, its 1:1 ratio with that of the *mmmr* pentad, and the low content of *rr*-type error all support a main stereoerror of the *mmmmrmmmm* type of relatively high abundance. This corresponds to polypropylene with stereoblock-isotactic microstructure (Figure 1, top) having short blocks, which is induced by frequent oscillation of the catalyst between its two enantiomeric forms, each catalyst enantiomer exhibiting significant propylene enantioface discrimination.

Increasing the concentration of monomer by conducting the polymerization in liquid propylene at room temperature retained the stereoblock-isotactic microstructure as revealed in the 1:1 ratio of the dominant *mmmr* and *mmrm* pentads in the ^{13}C NMR spectra. A higher degree of isotacticity revealed from the higher intensity of the *mmmm* pentad indicated that the blocks had become longer, consistently with the increase in the rate of monomer insertion relative to the rate of catalyst oscillation. The [{OSSO}Zr(Bn)$_2$]/MAO catalyst system yielded two fractions of stereoblock-isotactic polypropylene of [*mmmm*] = 42% (58 wt.-%, waxy solid soluble in hexane, average block length of ca. 8 repeat units) and [*mmmm*] = 57% (42 wt.-%, solid, insoluble in hexane, average block length of ca. 12 repeat units),[21] both featuring similar M_w and a narrow molecular weight distribution, supporting a similar catalytic species (Figure 2).[22] [{OSSO}Hf(Bn)$_2$]/MAO led to stereoblock-isotactic polypropylene with shorter blocks ([*mmmm*] = 26%, Figure 3). Since the hafnium complex is more rigid than the zirconium complex, this may seem counterintuitive. However, as the block length is determined by the ratio of insertion-to-flip rates, and since hafnium catalysts are usually slower than the analogous zirconium catalysts,[23,24] this result is, in fact, in line with expectations.

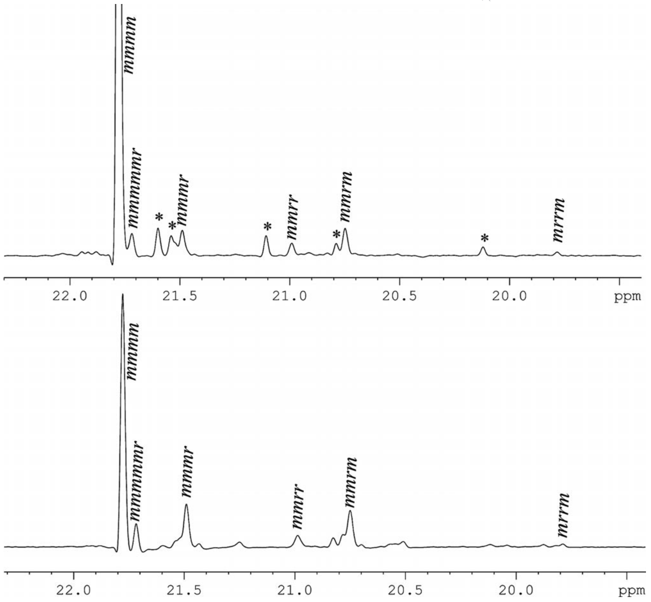


Figure 3. Methyl region of the ^{13}C NMR spectra of polypropylene prepared from liquid propylene with [{OSSO}Zr(Bn)$_2$]/MAO at room temperature (bottom, [*mmmm*] = 57%) and –10 °C (top, [*mmmm*] = 92%). Chain-end peaks designated with (*); for their assignment see the Supporting Information.

Polypropylene of higher isotacticity was obtained by using both catalysts in the polymerization of liquid propylene at –10 °C. The low M_w of the polypropylene that was obtained from the Zr catalyst enabled the detection of isobutyl, *n*-propyl, and vinylidene end groups in the ^{13}C NMR spectrum, which support a 1,2-insertion process and two termination processes: chain transfer to aluminum and β-H transfer.[25,26] For the Hf-derived polypropylene, [*mmmm*] was found to be 89%, and the only observable errors were the *mmmr*, *mmrr*, and *mrrm* pentads in an approximately 2:2:1 ratio, and the *mmrm* pentad, whose abundance was lower than that of the *mrrm* pentad (Figure 4, top). This indicates that the average distance between junctions of blocks of opposite stereochemistry has become so long (estimated as greater than or equal to 100 repeat units by comparing the *mmrm* and *mrrm* pentads) that the main stereoerror now is of the *mmmmrrmmmm* type (occurring every ca. 50 insertions; site enantioselectivity σ = 0.98).[27] This polymer is therefore best described as isotactic polypropylene, rather than stereoblock-isotactic polypropylene. A melting point of T_m = 141.2 °C is consistent with this degree of tacticity. For the polypropylene derived from the Zr catalyst at –10 °C, the degree of isotacticity was similar, but the amount of the *mmrm* pentad was considerably higher than that of the *mrrm* pentad, which is consistent with stereoblock-isotactic polypropylene having average block lengths of approximately 50 repeat units and a higher site enantioselectivity of $\sigma \geq 0.99$. The slightly lower melting point of this polymer of T_m = 136.8 °C may also reflect its lower molecular weight.[28] To the best of our knowledge, poly(α-olefins) having a stereoblock-isotactic microstructure, that is, consisting of isotactic blocks of opposite relative stereochemistry, whose blocks are of such high lengths (50 to above 100 repeat units) have never been constructed with a stand-alone catalyst (i.e., not equilibrating with a dormant species or assisted by a chain-transfer agent).

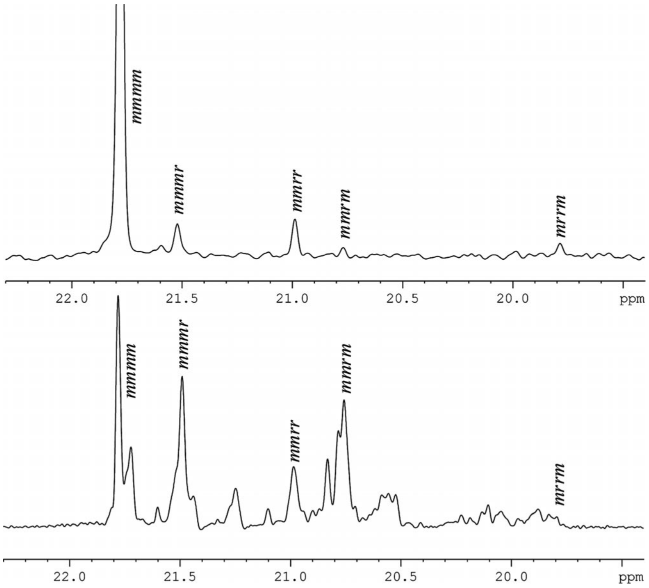


Figure 4. Methyl region of the ^{13}C NMR spectra of polypropylene prepared from liquid propylene with [{OSSO}Hf(Bn)$_2$]/MAO at room temperature (bottom, [*mmmm*] = 26%) and –10 °C (top, [*mmmm*] = 89%).

Conclusions

Polypropylene is often compared to a recording medium on which the signature of the catalyst is embedded. The fluxional zirconium and hafnium catalysts introduced herein carve two distinct signatures on the polymer backbone: the first one (*mmmmrmmmm*) dominating in the fast-oscillating regime and leading to a stereoblock-isotactic polypropylene, and the second one (*mmmmrrmmmm*) being revealed in the slow-oscillating regime with formation of isotactic polypropylene (Figure 5). We expect that modifications of the ligand backbone introduced herein may enable precise control of the oscillation rate and thereby of the microstructure of the polymers. Efforts in this direction are currently in progress in our group.

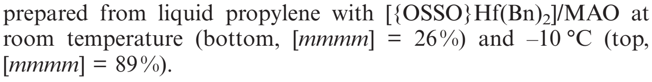


Figure 5. Microstructure of the polypropylene with the double signature of the oscillating catalysts: *mmmmrrmmmm* sequence signifying enantiomorphic site control (square frames) and *mmmmrmmmm* sequence signifying catalyst flip (round frame).

Supporting Information (see footnote on the first page of this article): Synthetic procedures and characterization of the ligand and the metal complexes, crystallographic data, polymerization procedures, and polymer characterization.

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[1] Fluxional complexes featuring a combination of a single-active conformation and inactive conformations (resting states) are not included in this definition.

[2] Fluxional catalysts in which the flip of the ligands and the insertion of the monomer are "geared" are a distinct class. For example, bis(phenoxyimine) titanium catalysts invert chirality-at-metal between (enantioselective) propylene insertions, which leads to syndiotactic polypropylene. See: H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.* **2011**, *111*, 2363 and references therein.

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[26] The low M_w of the polypropylene obtained at –10 °C is attributed to the substantial decrease in propagation rate (as may be inferred from the weight of polymer obtained; see Table S2 in the Supporting Information).

[27] For polypropylene of high isotacticity: the average block length in stereoblock-isotactic polypropylene is approximately $(0.5[mmrm])^{-1}$; the average distance between errors in isotactic polypropylene is approximately $(0.5[mmrr])^{-1} = ([mrrm])^{-1}$.

[28] Lower isotacticities were found for polymerization of liquid 1-hexene with {OSSO}Zr$(Bn)_2$/MAO and {OSSO}Hf$(Bn)_2$/MAO, which we attribute to the lower insertion rate of the bulkier monomer, giving the catalyst sufficient time to flip; see the Supporting Information.

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