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Stereoblock Polypropylene: Ligand Effects on the Stereospecificity of 2-Arylindene Zirconocene Catalysts

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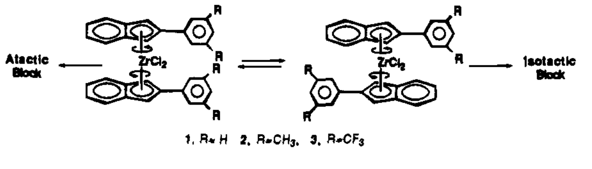
The control of stereochemistry in olefin polymerization is critical as the microstructure of polyolefins greatly influences their physical properties. Propylene polymerization with chiral racemic *ansa*-metallocenes yields highly crystalline isotactic polypropylenes while achiral catalyst precursors give amorphous atactic polymers.[1] Propylene polymers composed of blocks of atactic and isotactic stereosequences behave as thermoplastic elastomers. Natta discovered these polymers in the late 1950s and was the first to interpret their elastomeric properties in terms of stereoblock structure.[2] Two decades later, Collette and coworkers at DuPont described improved heterogeneous catalysts based on tetraalkyl group 4 catalysts.[3,4]

The first homogeneous catalyst system for the production of stereoblock polypropylene was a stereorigid chiral *ansa*-titanocene catalyst precursor reported by Chien.[5–7] Chien proposed a mechanism for this polymerization where enchainment of the monomer occurred sequentially at aspecific and isospecific coordination sites of the C_s-symmetric metallocene.[8,9] We have recently reported another strategy based on a nonbridged indenyl metallocene whose coordination geometry was designed to alternate between chiral and achiral forms during the course of the polymerization reaction (eq 1).[10] The metallocene, $(2\text{-PhInd})_2ZrCl_2$, **1** (PhInd = phenylindenyl), when activated by methylaluminoxane (MAO), generates catalysts which produce elastomeric polypropylenes.



(1)

We now report the effect of ligand modifications on the polymerization behavior of these nonbridged indenyl catalysts. The metallocene $(2\text{-PhInd})_2ZrCl_2$, **1**, was prepared as previously described.[10] The methyl-substituted compound **2** and the trifluoromethyl-substituted compound **3** were synthesized in an analogous manner from the reaction of 2-indanone and the corresponding aryl Grignard (**CAUTION**!).[11] ^1H and ^{13}C NMR spectra of all three zirconocenes at 25 °C reveal time-averaged molecular C_{2v} symmetry consistent with rapid rotation of the indenyl rings around the Cp(centroid)–Zr axis. This process could not be frozen out, even at −100 °C. Crystallization of complexes **2** and **3** from methylene chloride/hexane at −18 °C afforded crystals suitable for X-ray analysis (Figures 1 and 2).[12,13] As shown in Figure 1, the structure of **2** is closely isostructural with the *meso* rotamer previously reported for the 2-phenylindene derivative **1**. In contrast, complex **3** crystallizes in a racemic-like conformation. One common feature revealed by the crystal structures of all three compounds is the small dihedral angle (≤10°) between the planes defined by the indenyl ligands and the 2-aryl substituents.

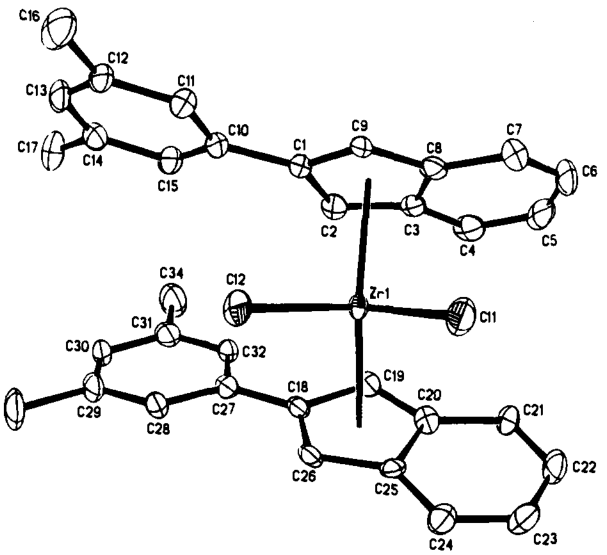


Figure 1. Molecular structure of complex **2**, showing atom-labeling scheme.

Complexes **1–3**, in the presence of MAO, produce active catalysts for propylene polymerization (Table 1). Catalysts derived from complex **2** are the least productive, while those derived from **1** exhibit slightly higher productivities than those derived from **3** at comparable polymerization pressures and temperatures. Polymers generated using complex **2** have lower molecular weights than those made using either **1** or **3**. The polydispersities obtained under these conditions are high (2.5–4) compared to what is typically observed for homogeneous systems (~2). Studies are underway to ascertain the origin of this behavior.

The most significant finding of the present study is the dramatic influence of the phenyl substituents on the microstructure of the resulting polymers. At 25 °C, complex **3** produces

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(1) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1143–1170.

(2) Natta, G. *J. Polym. Sci.* **1959**, *34*, 531–549.

(3) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851–3858.

(4) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858–3866.

(5) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030–2031.

(6) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G. Y.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 8569–8570.

(7) Babu, G. N.; Newmark, R. A.; Cheng, H. N.; Llinas, G. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 7400–7402.

(8) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771–3778.

(9) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779–3786.

(10) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217–219.

(11) (**CAUTION**: Trifluoromethyl aryl Grignards can explode! Appleby, I. C. *Chem. Ind.* **1971**, 120.) Complexes **2** and **3** were characterized fully by ^1H, ^{13}C NMR, X-ray, and microanalysis. See supporting information.

(12) Complex **2** selected bond lengths (Å): Zr(1)–Cl(1) 2.425(2), Zr(1)–Cl(2) 2.430(2), Zr(1)–C(1) 2.575(7), Zr(1)–C(2) 2.474(8), Zr(1)–C(3) 2.553(7), Zr(1)–C(8) 2.594(7), Zr(1)–C(9) 2.533(7), Zr(1)–C(18) 2.512(7), Zr(1)–C(19) 2.468(8), Zr(1)–C(20) 2.556(7), Zr(1)–C(25) 2.631(7), Zr(1)–C(26) 2.550(7), Zr(1)–Cnt(1) 2.240, Zr(1)–Cnt(2) 2.237. Selected angles (deg): Cl(1)–Zr(1)–Cl(2) 94.2(1), Cnt(1)–Zr(1)–Cnt(2) 130.1. Cnt(1) = centroid C(1)–C(2)–C(3)–C(8)–C(9), Cnt(2) = centroid C(18)–C(19)–C(20)–C(25)–C(26).

(13) Complex **3** selected bond lengths (Å): Zr(1)–Cl(1) 2.415(1), Zr(1)–Cl(2) 2.407(1), Zr(1)–C(1) 2.486(3), Zr(1)–C(2) 2.562(4), Zr(1)–C(7) 2.587(4), Zr(1)–C(8) 2.538(4), Zr(1)–C(9) 2.551(3), Zr(1)–C(18) 2.517(3), Zr(1)–C(19) 2.588(4), Zr(1)–C(24) 2.524(4), Zr(1)–C(25) 2.508(4), Zr(1)–C(26) 2.565(3), Zr(1)–Cnt(1) 2.400, Zr(1)–Cnt(2) 2.233. Selected angles (deg): Cl(1)–Zr(1)–Cl(2) 94.5(1), Cnt(1)–Zr(1)–Cnt(2) 130.9. Cnt(1) = centroid C(1)–C(2)–C(7)–C(8)–C(9), Cnt(2) = centroid C(18)–C(19)–C(24)–C(25)–C(26).

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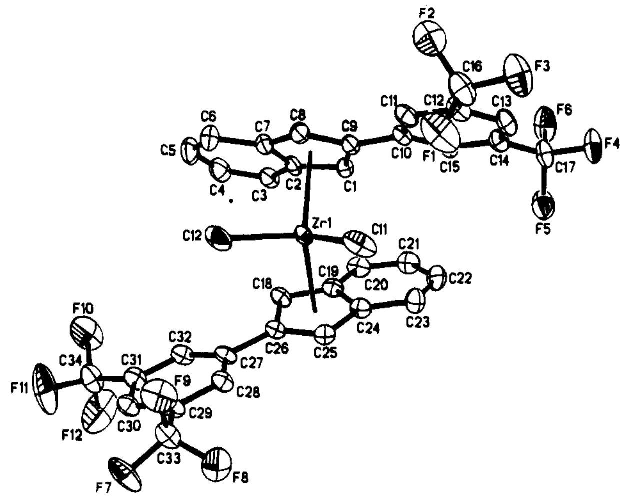

Figure 2. Molecular structure of complex **3**, showing atom-labeling scheme.

Table 1. Propylene Polymerizations Using Complexes **1**–**3** and MAO[a]

entry	catalyst	pressure (psig)	productivity[d] (×10^5)	M_w[e] (×10^3)	M_w/M_n	[m][f] (%)	[mmmm][f] (%)
1	**1**[b]	25	3.8	179	3.0	62	20
2		35	5.1	203	3.2	64	22
3		50	8.8	241	3.5	66	26
4		75	17.1	272	4.0	70	33
5		90	24.0	369	3.9	73	32
6	**2**[c]	35	1.5	81	2.5	62	15
7		50	2.2	129	2.6	62	18
8		75	3.6	166	2.7	65	23
9		90	5.4	174	2.7	66	24
10	**3**[c]	25	2.5	196	3.3	75	45
11		35	5.0	243	3.2	78	51
12		50	7.3	296	3.4	80	58
13		75	13.5	332	3.7	86	73

[a] Conditions: [Al]/[Zr]= 1000, $T = 25$ °C, $t = 60$ min. [b] [Zr]= 5.5 × 10^{-5} M. [c] [Zr]= 5.0 × 10^{-5} M. [d] Grams of polypropylene per mole of Zr per hour. [e] Determined by gel permeation chromatography versus polypropylene. [f] Determined by ^{13}C NMR spectroscopy.

polymers with a much higher percentage of isotactic pentads (45% ≤ [mmmm] ≤ 73%) than complexes **1** or **2** (15% ≤ [mmmm] ≤ 33%). We also observe an increase in isotactic pentads [mmmm] with increasing propylene pressure.[10] This effect is observed for all three of the catalysts studied, but is most pronounced for the trifluoromethyl-substituted catalyst **3**. This behavior, while unusual,[14–16] is predicted by the kinetic model proposed by Coleman and Fox for a two-site polymerization mechanism.[17,18]

Analysis of polypropylenes produced under similar conditions (50 psig, 25 °C, entries 3, 7, and 12) by IR spectroscopy[4,19] reveal that the isotactic helix content, as determined by the IR ratio A_{998}/A_{974}, increases in the order **2** (0.46) < **1** (0. 59) < **3** (0.72) (entries 7, 3, and 12, respectively).[20] This trend is also reflected in the thermal properties of these polypropylenes. For these same polymers we observe similar melting points but quite different enthalpies of fusion. For polymers from **2** (entry 7), $T_m = 137$ °C, $\Delta H = 0.2$ J/g; from **1** (entry 3), $T_m = 137$ °C, $\Delta H = 7.3$ J/g; and from **3** (entry 12), $T_m = 137$ °C, $\Delta H = 17.4$ J/g.[21,22] The high melting points ($T_m \sim 137$ °C) for materials with such low percentages of isotactic pentads (18% ≤ [mmmm] ≤ 73%) supports a blocky structure for these materials, as random copolymers with this range of isotacticities would be expected to have lower melting points.[23,24] Moreover, the variation in ΔH_{fusion} as a function of isotactic pentads and IR helix ratio suggests a corresponding increase in the degree of crystallinity. Tensile properties for samples run at larger scale under conditions similar to those of entries 5 and 13 are as follows: tensile strength = 857 psi (catalyst **1**), 5040 psi (catalyst **3**); elongation = 704% (catalyst **1**), 100% (catalyst **3**).

The origin of these dramatic ligand effects cannot be unambiguously established at this time. We postulate that isomerization of the catalyst by hindered rotation of the indenyl ligands[25] leads to an alternation in catalyst structure between achiral and chiral coordination geometries.[10] In the context of this mechanism, changes in ligand structure could affect the rate of olefin insertion, the rate of interconversion among the isomers, the steady-state equilibrium concentration of the various isomeric forms, or all of the above.[26] Studies to assess the relative roles of these factors are in progress.

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Supporting Information Available: Experimental details for the preparation of **2** and **3**, a typical polymerization procedure, and a complete description of the X-ray structure determination of complexes **2** and **3**, including atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) Ewen, J. W.; Elder, M. J.; Jones, R. L.; Curtis, S.; Cheng, H. N. *Stud. Surf. Sci. Catal.* **1990**, *56*, 439–482.

(15) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329–9330.

(16) Rieger, B.; Jany, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647–653.

(17) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065–1075.

(18) We note, however, that this kinetic model does not predict the observed increase in isotactic dyads [m] with propylene pressure, suggesting more complicated kinetic behavior than that predicted by a unimolecular catalyst isomerization process competing with a bimolecular polymerization step (see ref 10).

(19) Luongo, J. P. *J. Appl. Polym. Sci.* **1960**, *3*, 302–309.

(20) The IR ratio A_{998}/A_{974} is calculated from the absorptivities at 998 and 974 cm^{-1}. This is the inverse of the ratio reported by Luongo,[19] but is the same as that used by Collette.[4]

(21) For comparison, for typical commercial isotactic polypropylenes $T_m = 165$ °C; $\Delta H_f = 100$ J/g.

(22) For comparison, under identical polymerization conditions, (*R*,*S*)-ethylenebis(1-indenyl)$ZrCl_2$ produces isotactic polypropylene ([mmmm] = 85%) with $T_m = 136$ °C, $\Delta H = 52.7$ J/g.

(23) Newman, S. *J. Polym. Sci.* **1960**, *47*, 111–137.

(24) Cheng, S. Z.; Janimak, J. J.; Zhang, A.; Hsieh, E. T. *Polymer* **1991**, *32*, 648–55.

(25) Recent reports of cyclopentadienyl-hindered rotations have appeared. See, for example: Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590–4601. Sitzmann, H.; Zhou, P.; Wolmershäuser, G. *Chem. Ber.* **1994**, *127*, 3 and references therein.

(26) Several studies dealing with substituent effects on the polymerization behavior of Ziegler Natta catalysts have appeared. See, for example: Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954. Lee, I.-M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.