

# Propylene Polymerization with Sterically Hindered Unbridged 2-Arylindenyl Metallocenes

Gregg M. Wilmes, Shirley Lin, and Robert M. Waymouth\*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received December 26, 2001; Revised Manuscript Received March 26, 2002

**ABSTRACT:** Metallocene catalyst systems derived from bis(2-phenylindenyl)zirconium dichloride (**1**) yield elastomeric polypropylenes of low to intermediate tacticity. The sterically hindered metallocene bis(2-(3,5-di-*tert*-butylphenyl)indenyl)zirconium dichloride (**2**) produces polypropylenes of much higher isotacticity than **1** ([mmmm] = 78% vs 44% in liquid propylene). Kinetic profiles of polymerizations conducted with **1**/MMAO and **2**/MMAO reveal that the initial rates of polymerization increase with increasing temperature; the activity of both catalysts decreases with time, but the decrease is less pronounced for **2**/MMAO than for **1**/MMAO. The polymer microstructure is highly dependent upon polymerization conditions: isotacticity decreases with increasing temperature and decreasing monomer concentration. Lower tacticity polypropylenes ([mmmm] = 40%) generated with **2**/MMAO at low monomer concentrations contain a high percentage of [mmrm] stereoerrors, which is indicative of a stereoblock microstructure comprised of isotactic stereosequences of opposite relative configuration. Activation of bis(2-(3,5-di-*tert*-butylphenyl)indenyl)zirconium dimethyl (**3**) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**4**) or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**5**) yielded catalysts with quite different polymerization behavior. A modest drop in productivity and isotacticity in propylene polymerization is observed when **3** is activated with **4**, relative to MMAO, but catalysts derived from **3**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> exhibited low productivity and afforded amorphous polypropylenes of very low tacticity ([mmmm] = 12%).

## Introduction

The stereoselective polymerization of propylene with metallocene catalysts has resulted in the synthesis of new classes of polypropylenes and provided insights into the details of stereoselective polymerization reactions.<sup>1–3</sup> Isotactic polypropylene, an important industrial thermoplastic, is produced by both traditional Ziegler–Natta type catalysts and, more recently, by metallocene catalyst systems. An attractive feature of metallocene catalysts is their ability to generate polypropylenes of lower tacticity in order to modulate the crystallinity, density, and physical properties of the resulting polymers.<sup>2</sup> For the past several years, we have been investigating a family of conformationally dynamic metallocene systems in an effort to control the number and distribution of atactic stereocenters in polypropylene.<sup>4–13</sup> Some of these low-tacticity polypropylenes have elastomeric properties<sup>14–18</sup> and yet retain the high melting temperatures of more crystalline isotactic polypropylenes.

We have proposed that the low to intermediate tacticities of polypropylenes prepared by unbridged 2-arylindenyl metallocene catalysts such as bis(2-phenylindenyl)zirconium dichloride (**1**) is a consequence of the competition between propylene enchainment and the conformational dynamics of the catalyst. Interconversion between a stereoselective anti conformation and a nonstereoselective syn conformation was proposed as a means of generating blocks of atactic and isotactic stereosequences in a single polymer chain as shown in Scheme 1 (here we have explicitly included both enantiomers of the chiral anti (*rac*) isomers; vide infra).

The strong sensitivity of these catalyst systems to the nature of the ligands and the polymerization conditions offers the possibility of tuning these catalysts to prepare

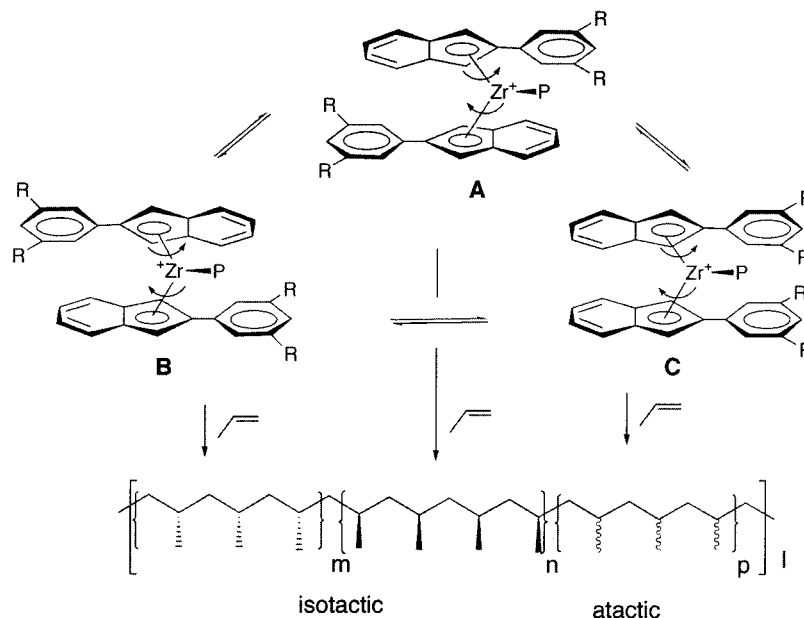
a wide variety of polypropylene microstructures. One strategy that we have employed<sup>5,6,19</sup> is to introduce ligand substitutions that might bias the conformational equilibria toward the more stereospecific conformations. This can be done by introduction of electronically biased<sup>5,6</sup> or sterically biased<sup>19,20</sup> metallocenes that favor the anti conformations. In this contribution, we detail our investigations on the polymerization behavior of a modified 2-arylindenyl metallocene, bis(2-(3,5-di-*tert*-butylphenyl)indenyl)zirconium dichloride ((2-(3,5-*t*-Bu<sub>2</sub>-Ph)Ind)<sub>2</sub>ZrCl<sub>2</sub>) (**2**), under a variety of polymerization conditions. Metallocene **2** produces polypropylenes of higher isotacticity and molecular weight and exhibits a higher activity than **1** at 60 °C. Analysis of the dependence of polymer microstructure on monomer concentration at 20 °C for **2**/MMAO suggests that the two enantiomeric anti conformations interconvert in competition with enchainment; the syn rotamer may not be accessible to these sterically hindered metallocenes.

## Results

**Synthesis.** Metallocene **1** was prepared as previously described. Metallocene **2** was prepared in 64% yield by metalation of ZrCl<sub>4</sub> with the lithium salt of 2-(3,5-di-*tert*-butylphenyl)indene in diethyl ether.<sup>21,22</sup> The ligand 2-(3,5-di-*tert*-butylphenyl)indene was prepared in 70% yield from 2-indanone and 3,5-di-*tert*-butylbenzene-1-magnesium bromide in diethyl ether. 1-Bromo-3,5-di-*tert*-butylbenzene was prepared in 29% yield by the bromination of 1,3,5-tri-*tert*-butylbenzene in carbon tetrachloride.<sup>23</sup> The dimethyl analogue of **2**, (2-((3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub>) (**3**), was prepared from **2** by treatment with methyllithium in diethyl ether.

**Influence of Polymerization Temperature.** The polymerization of propylene was carried out with **1**/MMAO and **2**/MMAO in toluene solution ([C<sub>3</sub>H<sub>6</sub>] = 1.2 M) and bulk monomer at 20, 40, and 60 °C (Table

\* Corresponding author. E-mail: waymouth@stanford.edu.

**Scheme 1. Proposed Mechanism for Propylene Enchainment by 2-Arylindene Metallocenes****Table 1. Propylene Polymerizations at Various Temperatures Using 1/MMAO and 2/MMAO<sup>a</sup>**

entry	catalyst	[C <sub>3</sub> H <sub>6</sub> ] (M)	<i>P</i> (psig)	<i>T<sub>p</sub></i> (°C)	<i>r</i> <sub>max</sub> (mmol/min)	[mmmm] <sup>b</sup>	<i>M<sub>n</sub></i> (g/mol) <sup>c</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup>
1	<b>1</b>	11 <sup>d</sup>	n/a	20	nd <sup>e</sup>	0.44	100 000	3.0
2	<b>1</b>	1.2	10	20	0.63	0.18	35 700	2.6
3	<b>1</b>	1.2	24	40	0.67	0.09	11 200	2.4
4	<b>1</b>	1.2	48	60	0.78	0.05	3 900	2.2
5	<b>2</b>	1.2	10	20	nd <sup>e</sup>	0.40	70 700	2.8
6	<b>2</b>	1.2	24	40	0.66	0.29	31 900	4.8
7	<b>2</b>	1.2	48	60	1.37	0.17	13 600	4.1

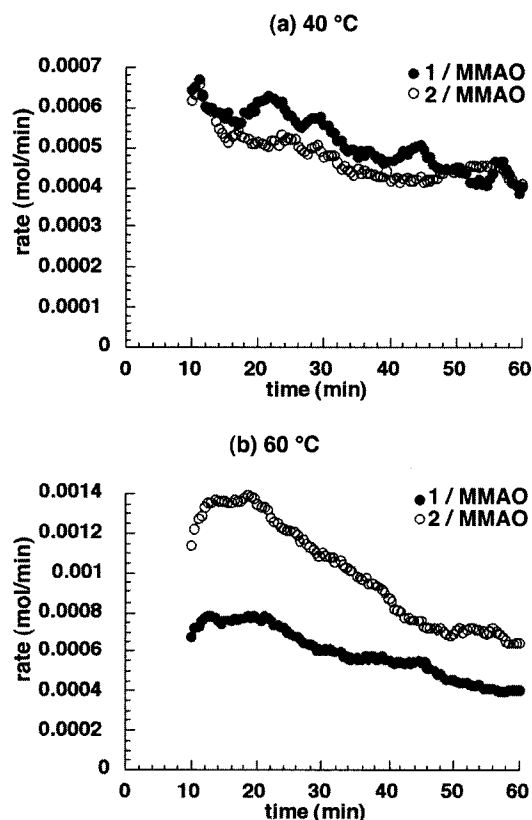
<sup>a</sup> Polymerization conditions: [Zr] =  $1.0 \times 10^{-5}$  M; [Al]/[Zr] = 3160; [C<sub>3</sub>H<sub>6</sub>] = 1.16 M; *t*<sub>rxn</sub> = 60 min. <sup>b</sup> By <sup>13</sup>C NMR. <sup>c</sup> By high-temperature GPC. <sup>d</sup> Synthesized in 90 mL of liquid propylene + 10 mL of toluene. <sup>e</sup> Not determined.

1). The solubility of propylene in toluene was determined at 40 and 60 °C in a manner described previously.<sup>7</sup> At a given monomer concentration, an increase in the polymerization temperature results in an increase in the maximum rate of polymerization, a decrease in the molecular weight, and a decrease in isotacticity of the resulting polypropylenes for metallocenes **1** and **2** (Table 1). For metallocene **1**, low molecular weight atactic polypropylene is obtained from polymerizations carried out at 60 °C at 1.2 M propylene.

Comparable rates of polymerization are observed for metallocenes **1** and **2** at 40 °C, but at 60 °C metallocene **2** is more active than **1** (Table 1 and Figure 1). The rate profiles<sup>7</sup> shown in Figure 1 reveal that the polymerization rate at 40 °C for catalysts derived from both **1** and **2** reach a maximum after approximately 10 min and then decrease over the next 50 min. At 60 °C, the rate of polymerization for metallocene **2** is higher than that of **1** but decreases more rapidly.

Both metallocenes yield polypropylenes of intermediate tacticity, but metallocene **2** yields more highly isotactic polymers than those of **1** under all conditions investigated: at 20 °C [mmmm] = 18% for polypropylenes synthesized by **1** vs [mmmm] = 40% for **2** ([C<sub>3</sub>H<sub>6</sub>] = 1.2 M, Table 1, entries 2, 5). The molecular weight distribution of polymers synthesized by **2**/MMAO are comparable to those of **1**/MMAO at 20 °C but are higher at higher polymerization temperatures: *M<sub>w</sub>*/*M<sub>n</sub>* > 4.0 at 40 and 60 °C.

**Influence of Monomer Concentration.** Propylene polymerizations with **2**/MMAO were conducted at seven different monomer concentrations ([C<sub>3</sub>H<sub>6</sub>] = 1.2–11 M)

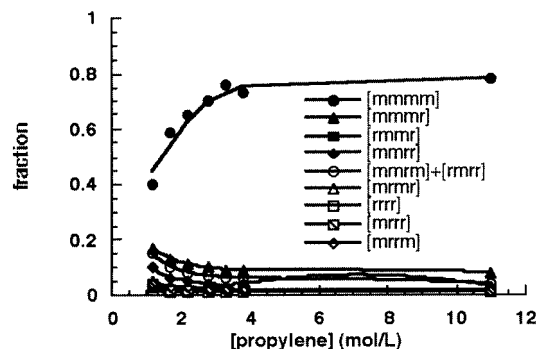


**Figure 1.** Comparison of catalyst activity between (2-PhInd)<sub>2</sub>ZrCl<sub>2</sub> (**1**/MMAO) and (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrCl<sub>2</sub> (**2**/MMAO) at (a) 40 °C and (b) 60 °C.

**Table 2.** Pentad Distributions of Polypropylenes Synthesized at Various Monomer Concentrations Using 2/MMAO<sup>a</sup>

entry	[C <sub>3</sub> H <sub>6</sub> ] (M)	prod <sup>b</sup>	M <sub>n</sub> (g/mol) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	T <sub>m,max</sub> (°C) <sup>d</sup>	ΔH <sub>f</sub> (J/g) <sup>d</sup>	[mmmm] <sup>e</sup>	[mmmr]	[rmmr]	[mmrr]	[mmrm] +[rmrr]	[mrmm]	[rrrr]	[mrrr]	[mrrm]
8	1.2	4000	70 700	2.8	45, 120	27.9	0.40	0.17	0.03	0.10	0.15	0.05	0.02	0.04	0.04
9	1.7	1890	100 000	3.2	45, 130	58.0	0.59	0.13	0.02	0.06	0.10	0.03	0.01	0.02	0.03
10	2.2	2490	90 100	3.2	46, 140	60.5	0.65	0.11	0.02	0.05	0.08	0.03	0.01	0.02	0.03
11	2.7	2020	154 000	3.5	51, 149	75.2	0.70	0.10	0.02	0.04	0.07	0.02	0.01	0.01	0.02
12	3.3	2420	162 000	3.6	145	64.4	0.76	0.09	0.01	0.03	0.06	0.02	0.01	0.01	0.02
13	3.8	4850	119 000	3.3	45, 144	67.6	0.75	0.09	0.01	0.04	0.06	0.02	0.00	0.01	0.02
14	11 <sup>f</sup>	2140	64 700	3.8	155	93.0	0.78	0.08	0.02	0.03	0.04	0.01	0.01	0.01	0.01

<sup>a</sup> Polymerization conditions: [Zr] =  $2.0 \times 10^{-6}$  M; [Al] =  $3.16 \times 10^{-2}$ ; [Al]/[Zr] = 15 800; T<sub>p</sub> = 20 °C; t<sub>rxn</sub> = 60 min. <sup>b</sup> Productivity in kg PP/(mol Zr h). <sup>c</sup> By high-temperature GPC. <sup>d</sup> By DSC. <sup>e</sup> By <sup>13</sup>C NMR. <sup>f</sup> Synthesized in 90 mL of liquid propylene + 10 mL of toluene.

**Figure 2.** Plot of pentad fraction vs propylene concentration for (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO (2/MMAO).

using the procedure previously described<sup>7</sup> (Table 2). Under these conditions, the productivities varied and did not show a clear trend. For polymerizations in solution (entries 8–13, Table 2), the molecular weights were greater than those of the polymer obtained in liquid monomer (~11 M). Molecular weight distributions were broader ( $M_w/M_n = 2.8$ – $3.8$ ) than those of polypropylenes synthesized by 1/MMAO where  $M_w/M_n = 2.0$ – $2.6$ .<sup>7</sup>

The microstructure of the polypropylenes produced with metallocene **2** is quite sensitive to monomer concentration, a characteristic of other metallocenes of this class.<sup>7</sup> As shown in Table 2 and Figure 2, [mmmm] decreases from 78% to 40% as monomer concentrations decrease from 11 to 1.2 M. This decrease in [mmmm] occurs abruptly at propylene concentrations below approximately 4 M and is accompanied by increases in the [mmmr], [rmmr], [mmrr], and [mrrm] pentads (Table 2). DSC thermograms of the polymers in Table 2 reveal very broad melting endotherms for polymers exhibiting crystallinity, another feature of polypropylenes synthesized by unbridged 2-arylindene catalysts.<sup>24,25</sup> The degree of crystallinity of the polymers increases with increasing tacticity (and increasing monomer concentration) as reflected in the heats of fusion, ΔH<sub>f</sub>.

**Effect of Cocatalyst on Propylene Polymerizations with (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub>.** Polymerizations were conducted in toluene with (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub> (**3**) activated by MMAO, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**4**), or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**5**) and in bulk propylene with **4**. Triisobutylaluminum (TIBA) was added to each run to scavenge impurities. The polymers obtained were analyzed by <sup>13</sup>C NMR, DSC, and high-temperature GPC (Tables 3 and 4). As observed for polymerizations using (2-PhInd)<sub>2</sub>ZrMe<sub>2</sub>,<sup>12</sup> the nature of the cocatalyst has a dramatic influence on the microstructure of the polypropylenes obtained from **3**. Activation of **3** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> **5** yielded a very low-tacticity polypropylene ([mmmm] = 12%, entry 15, Table 3) under conditions in which the MMAO cocatalyst yielded an isotactic polypropylene

([mmmm] = 70%, entry 16, Table 3). The productivity of the catalyst system derived from **5** was also considerably lower than those for other activators. Polypropylenes obtained from cocatalyst **4** were also less isotactic and less crystalline than those from systems activated by MMAO ([mmmm] = 47% vs 70%; ΔH<sub>f</sub> = 54 vs 76 J/g at [C<sub>3</sub>H<sub>6</sub>] = 2.7 M; entries 18 and 16, Table 3). However, for the catalyst system **3**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], the tacticity of the polypropylenes increased with increasing monomer concentration in a manner similar to 2/MMAO.

## Discussion

Conformationally dynamic metallocene catalysts based on 2-arylindenyl metallocenes are remarkably versatile catalyst systems that can generate a wide range of polypropylene microstructures (6% < [mmmm] < 76%). These catalyst systems are very sensitive to ligand variations and polymerization conditions. Polypropylenes of low to intermediate tacticity (19% < [mmmm] < 50%) generated from this family of metallocenes exhibit elastomeric properties; the properties of these materials depend quite sensitively on their microstructure.<sup>13,24,25</sup>

A characteristic feature of this class of metallocenes is the strong influence of substituents on the 3,5-positions of the 2-aryl substituent on the stereoselectivity of the catalysts.<sup>5,6,19</sup> Metallocenes containing a 3,5-dimethylphenyl substituent yield polypropylenes with similar microstructures to **1**, whereas those substituted with either trifluoromethyl (bis(2-(3,5-difluoromethylphenyl)indenyl)zirconium dichloride **6**) or *tert*-butyl groups (bis(2-(3,5-di-*tert*-butyl-4-methoxyphenyl)indenyl)zirconium dichloride **7**) yield propylenes of much higher tacticity.<sup>5,6,19</sup> The different stereoselectivities observed for differently substituted metallocenes can be attributed to many factors, including (1) the accessibility of the various conformations, (2) the stereospecificity of any given conformation, (3) the relative rate at which these conformations interconvert relative to the rate of polymer chain propagation, and (4) the equilibria among the different accessible conformations.<sup>5</sup> Our efforts in preparing sterically hindered metallocenes (**2** and **7**) or those with strong dipoles (**6**) were guided by the hypothesis that steric or electronic effects might bias the steady-state equilibria among various conformations toward the more stereospecific conformations to generate more highly tactic polypropylenes. The higher stereospecificities of the 3,5-disubstituted metallocenes **2**, **6**, and **7** are consistent with the interpretation that conformations that lead to isotactic stereosequences (the anti rotamers of Scheme 1) are either more active or more frequently populated than conformations leading to atactic stereosequences.

The dependence of catalyst stereoselectivity on monomer concentration is a signature of a mechanism involv-

**Table 3. Propylene Polymerizations with (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub><sup>a</sup> (3)**

entry	[C <sub>3</sub> H <sub>6</sub> ] (M)	activator <sup>b</sup>	[Zr] (μM)	prod <sup>c</sup>	[mmmm] <sup>d</sup>	<i>M<sub>n</sub></i> (g/mol) <sup>e</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>e</sup>	<i>T<sub>m,max</sub></i> <sup>f</sup> (°C)	Δ <i>H<sub>f</sub></i> <sup>g</sup> (J/g)
15	2.7	<b>5</b>	190	290	0.12	76 900	2.4	nd <sup>g</sup>	nd <sup>g</sup>
16	2.7	MMAO	6.0	3180	0.70	124 000	3.6	49, 144	76
17	1.2	<b>4</b>	6.0	560	0.29	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>
18	2.7	<b>4</b>	6.0	2160	0.47	80 000	2.9	47, 130	34
19	3.8	<b>4</b>	6.0	3340	0.52	115 000	3.2	49, 135	54
20	11 <sup>i</sup>	<b>4</b>	6.0	1450	0.58	88 400	2.9	54, 150	46

<sup>a</sup> Polymerization conditions: [MMAO]/[Zr] = 15 800; [B]/[Zr] = 1; 252 μmol TIBA; *T<sub>p</sub>* = 20 °C, *t<sub>rxn</sub>* = 30 min. <sup>b</sup> **4** = [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], **5** = B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. <sup>c</sup> Productivity in kg of PP/(mol Zr h). <sup>d</sup> By <sup>13</sup>C NMR. <sup>e</sup> By high-temperature GPC. <sup>f</sup> By DSC. <sup>g</sup> None detected. <sup>h</sup> Not determined. <sup>i</sup> Polymer synthesized in 90 mL of liquid propylene + 10 mL of toluene.

**Table 4. Full Pentad Distribution<sup>a</sup> of Polypropylenes Synthesized by (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub> (3) with Various Activators**

entry <sup>b</sup>	[C <sub>3</sub> H <sub>6</sub> ] (M)	activator <sup>c</sup>	[mmmm] <sup>c</sup>	[mmmr]	[rmmr]	[mmrr]	[mmrm]+ [rmrr]	[mrmm]	[rrrr]	[mrrr]	[mrrm]
15	2.7	<b>5</b>	0.12	0.16	0.07	0.13	0.23	0.11	0.04	0.10	0.04
16	2.7	MMAO	0.70	0.10	0.02	0.05	0.07	0.02	0.01	0.02	0.02
17	1.2	<b>4</b>	0.29	0.17	0.05	0.10	0.19	0.08	0.03	0.06	0.05
18	2.7	<b>4</b>	0.47	0.15	0.03	0.07	0.14	0.05	0.02	0.03	0.03
19	3.8	<b>4</b>	0.52	0.15	0.03	0.06	0.13	0.04	0.02	0.02	0.03
20	11	<b>4</b>	0.58	0.14	0.03	0.06	0.12	0.03	0.01	0.02	0.02

<sup>a</sup> By <sup>13</sup>C NMR. <sup>b</sup> Entry numbers from Tables 3 and 4 correspond to the same polypropylene samples. <sup>c</sup> **4** = [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], **5** = B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

ing some process that competes with the stereodifferentiating step. The strong concentration dependence on the stereoselectivity for metallocene **2** (Table 2) implies that a similar competition between insertion and isomerization exists in this case. For these sterically hindered metallocenes, isomerization between the two enantiomeric anti conformations is still possible. A detailed examination of the microstructure of polymers synthesized by **2** at a variety of monomer concentrations supports this hypothesis. This metallocene yields isotactic polypropylenes at high monomer concentrations and lower tacticity polypropylenes at low monomer concentrations. At a monomer concentration of 1.2 M, metallocene **2** yields a polypropylene of intermediate tacticity ([mmmm] = 40%, entry 8, Table 2). Investigation of the pentad distribution reveals stereodefects derived predominantly from [mmmr], [mmrm], and [mmrr] pentads; the percentage of the [mmrr] pentad, characteristic of atactic sequences, is negligible. These results suggest that the stereodefects are primarily isolated stereoerrors rather than blocks of stereoerrors. The origin of the isolated [mmrm] stereoerrors could be ascribed either to a low stereospecificity for the stereoselective conformers or to the epimerization of the last inserted stereocenters of the growing chain.<sup>26–30</sup> The fact that the concentration of [mmrr] and [mmrm] stereoerrors increases with decreasing monomer concentration suggests that epimerization is a likely origin of these stereodefects.

The presence of a relatively high concentration of [mmrm] stereoerrors is consistent with a microstructure containing a significant fraction of isotactic sequences of opposite configuration separated by isolated [r] diads. The increase in [mmrm] pentads with decreasing monomer concentration suggests that the length of the isotactic blocks separated by these isolated [r] diads decreases with decreasing monomer concentration. These results imply that isomerization takes place primarily between the two enantiomeric anti (*rac*) conformations, **A** and **B**, of these sterically hindered metallocenes, leading to an isotactic stereoblock structure (Scheme 1, *p* = 0), similar to that proposed by Kaminsky for polypropylenes derived from bis(neomenthylcyclopentadienyl)ZrCl<sub>2</sub>.<sup>31–33</sup> For the sterically hindered metallocene **2**, it is possible that the syn rotamer **C**, with

the 2-aryl rings in a near-eclipsed conformation, is destabilized to the point where it is no longer populated or kinetically competent to enchain the monomer. This is consistent with recent theoretical studies that the anti conformations are more stable than the syn for both **1** and **2** but that the difference is much more pronounced for **2**.<sup>20</sup>

The observation of a significant fraction of [mmrm] stereoerrors in polymers derived from **2** suggests that the direct interconversion of the enantiomeric anti forms is an important component of the conformational dynamics of these systems (Scheme 1) and that the mechanistic picture for these metallocenes should include at least three states (additional conformations are of course possible) where the metallocene can interconvert between the two enantiomeric anti conformations **A** and **B** as well as the achiral syn conformation **C**. A similar conclusion was recently suggested by Busico through analysis of the high-resolution <sup>13</sup>C NMR spectra of polymers derived from **7** at heptad resolution.<sup>34,35</sup> The implication that the achiral syn rotamer does not contribute significantly to the polymerization behavior of **2** raises the possibility that a similar situation exists for catalysts based on (2-PhInd)<sub>2</sub>ZrCl<sub>2</sub>, **1**. Previous studies with bridged metallocenes<sup>8</sup> have provided evidence that the syn rotamer of metallocene **1** is competent to enchain the monomer, and analysis of the microstructure of polymers derived from **1** is consistent with the presence of long atactic stereosequences.<sup>24,34</sup> Kinetic modeling implies that for **1** the rates of insertion relative to isomerization differ only by a factor of 10 (depending on the monomer concentration).<sup>7,36</sup> If there is a distribution of relative rates for these two processes, it is possible that these metallocenes also isomerize only between the enantiomeric forms **A** and **B** and that the atactic stereosequences in the polymers are due to populations of kinetic states where the rates of olefin insertion are slower than the rate of isomerization (Curtin–Hammett conditions). Although we have no direct evidence at this time to differentiate between the contribution of a syn rotamer and the performance of the catalyst under Curtin–Hammett conditions, the similarity (at pentad resolution) between the <sup>13</sup>C NMR spectra of two polypropylenes of comparable tacticity, one synthesized with **1** in liquid propylene ([mmmm] =



44%, entry 1, Table 1) and one made with **2** at low monomer concentration ( $[\text{mmmm}] = 40\%$ , entry 8, Table 2), reveals that lower tacticity elastomeric polypropylenes are accessible from either the unsubstituted **1** or the *tert*-butyl-substituted **2** under appropriate conditions. Further studies are warranted to assess the role of the syn rotamers in generating the atactic stereosequences in these polymers.

In addition to the influence on the stereospecificity, the nature and position of the substituents on the 2-phenyl ligand also influence other aspects of the polymerization behavior. The molecular weights of polymers produced by **2**/MMAO are higher than those derived from **1**/MMAO. Both metallocenes show a decrease in molecular weight with increasing polymerization temperature (Table 1), but for **1**, this effect is quite dramatic, leading to a low molecular weight, atactic polypropylene at 60 °C. Introduction of *t*-Bu groups on the phenyl rings also appears to influence the temperature performance of these catalysts. While the rates of polymerization at 40 °C are comparable for **1** and **2**, metallocene **2** shows a higher rate at 60 °C than **1**.

The nature of the cocatalyst system also has a significant influence on the polymerization behavior of these metallocene catalysts. Activation of the dimethyl derivative (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrMe<sub>2</sub> (**3**) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TIBA yields an atactic polypropylene ( $[\text{mmmm}] = 12\%$ ) under conditions where activation by MMAO yields a highly isotactic polypropylene ( $[\text{mmmm}] = 70\%$ ). In a separate contribution, we have shown that the stereoselectivity of the dimethyl derivative of metallocene **1** is much lower in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TIBA<sup>12</sup> than in MMAO, but the magnitude of change for **2** is quite remarkable—this highly stereoselective catalyst system is transformed to a stereorandom one in the presence of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TIBA cocatalyst system! Activation of **3** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (**4**) also yields less isotactic polypropylene than that obtained in the presence of MMAO (entries 18 and 16, Table 3). The strong dependence of the stereoselectivity on the nature of the cocatalyst implies that the nature of the ion pairs formed in the activated complexes has a strong influence on the polymerization behavior of these catalyst systems, even for these sterically hindered systems.<sup>12,35</sup> Possible origins of these effects include ion-pairing phenomena that influence (1) the relative population and/or activity of accessible conformations, (2) the stereospecificity of any given conformation, or (3) the relative rate at which these conformations interconvert relative to the rate of polymer chain propagation. The increase in tacticity with increasing monomer concentration for the **3**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA catalyst system implies that the conformational dynamics competes with olefin insertion, as observed with MMAO cocatalyst. The lower stereoselectivity of catalysts derived from **3**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (Table 3) relative to MMAO might be explained by change in the relative rates of propagation and isomerization. Since the productivities are comparable (entries 16 and 18), this may imply a higher rate of conformational isomerism with this cocatalyst system. Further studies are underway to address this possibility.

For the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> cocatalyst system, we posit that the strongly coordinating CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> anion decreases the rate of propylene insertion<sup>37,38</sup> to the point that the rate of olefin insertion becomes competitive with isomeriza-

tion, leading to short isotactic block lengths and a more stereorandom microstructure.<sup>12</sup> The significantly lower productivity of the catalyst system derived from **3**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is consistent with this interpretation. The high sensitivity of these 2-arylindene catalyst systems to both ligand effects and polymerization conditions allows for a wide range of polymer structures to be prepared.

## Conclusions

The sterically hindered metallocene bis(2-(3,5-di-*tert*-butylphenyl)indenyl)zirconium dichloride (**2**), when activated with MMAO, produces polypropylenes of much higher isotacticity than the metallocene (2-PhInd)<sub>2</sub>ZrCl<sub>2</sub> (**1**). Analysis of the pentad content of low-tacticity polypropylenes generated with **2**/MMAO at low monomer concentrations is consistent with a stereoblock microstructure comprised of isotactic stereosequences of opposite relative configuration, implicating the interconversion of two enantiomeric anti rotamers in competition with olefin insertion. The strong dependence of the tacticity on the nature of the cocatalyst implies that catalyst/cocatalyst interactions provide another means of modulating the stereospecificity of these conformationally dynamic systems. By varying the polymerization conditions (monomer concentration, temperature, and cocatalyst), this class of catalysts can produce a wide variety of polypropylene microstructures.

## Experimental Section

The metallocene (2-phenylindenyl)<sub>2</sub>ZrCl<sub>2</sub> was synthesized according to literature procedure and used in elementally pure form.<sup>4</sup> MMAO was obtained from AKZO (AKZO MMAO Type 4) and was dried in vacuo prior to use. Procedures for determination of propylene solubility in toluene at 40 and 60 °C as well as for conducting polymerizations were identical to the experimental procedures previously described.<sup>7</sup> <sup>13</sup>C NMR of the polymers synthesized were collected using a 75 MHz Varian Inova spectrometer. Samples were prepared using C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>/C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> and data collected at 100 °C. Polymer molecular weights were measured using a Waters 150-C ALC/GPC at 139 °C in 1,2,4-trichlorobenzene vs polypropylene standards. Differential scanning calorimetry was performed using a Perkin-Elmer DSC 7. Polymer samples were annealed at 180 °C for 10 min, cooled to 20 °C at a rate of 10 deg/min, and allowed to rest at room temperature for 36 h. Heating curves were measured with a heating rate of 20 deg/min from 20 to 180 °C.

**Preparation of Bromo-3,5-di-*tert*-butylbenzene.**<sup>23</sup> 1,3,5-Tri-*tert*-butylbenzene (150 g, 0.6 mol) was dissolved in carbon tetrachloride (300 mL) in a three-necked flask which had been painted black to avoid light and equipped with an overhead stirrer, thermometer, and addition funnel under argon. Iron pellets (36 g, 0.64 mol) were added, and the slurry was cooled to 5 °C. *tert*-Butylcatechol (1.0 g) was added, and a solution of bromine (201.6 g, 1.26 mol) in carbon tetrachloride (75 mL) was added over a 1 h period. The slurry was stirred for an additional 4 h at 5 °C and quenched by pouring into ice water. The layers were separated, and the organics were washed with 10% sodium hydroxide solution. The solution was then washed with salt brine and dried over magnesium sulfate. The solvent was evaporated, and the product was distilled under vacuum twice to give 75 g of product, which was then recrystallized from heptane to give 47 g of pure product (29%).

**Preparation of 2-(3,5-di-*tert*-Butylphenyl)indene.**<sup>21,22</sup> 1-Bromo-3,5-di-*tert*-butylbenzene (47.2 g, 0.175 mol) was dissolved in ether (500 mL) and cooled to −70 °C. *tert*-Butyllithium (200 mL of 1.7 M solution in pentane, 0.34 mol) was added at −70 °C over a 2 h period. The solution was allowed to warm to room temperature slowly. Magnesium bromide etherate (46.5 g, 0.18 mol) was added, and the slurry was stirred for 1 h. The mixture was then cooled to 5 °C, and

2-bromoindene (34.2 g, 0.18 mol) was added. The mixture was warmed to room temperature and then refluxed for 3 h. The solution was cooled to room temperature, and the reaction was quenched carefully with water. The layers were separated, and the organics were washed with salt brine and dried over magnesium sulfate. The solvents were evaporated, and the product was distilled twice and recrystallized from hexane to give 37.1 g of product (70%).

**Preparation of Bis(2-(3,5-di-*tert*-butylphenyl)indenyl)-zirconium Dichloride.** 2-(3,5-Di-*tert*-butylphenyl)indene (13.8 g, 0.045 mol), and anhydrous diethyl ether (250 mL) were placed in a 1 L three-necked flask under argon. *n*-Butyllithium (28 mL of a 1.6 M solution in hexanes, 0.045 mol) was added over a 30 min period at 0 °C. The solution was stirred for an additional 2 h. Zirconium tetrachloride (5.1 g, 0.022 mol), was added incrementally over a 1 h period. The mixture was then stirred overnight. The ethereal solution was chilled to -10 °C, and the solids were collected. The solids were taken up in 300 mL of dichloromethane, and the residual solids were removed by filtration through Celite. The Celite was washed with an additional 100 mL of dichloromethane, and the solvents were evaporated to give 11.2 g of product (64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 293 K): δ 7.61 (s, 4 H, Ph-2,6) 7.56 (s, 2 H, Ph-4) 7.00 (dd, 4 H, *J* = 6.5 Hz, *J* = 2.9 Hz, Ind-4,5) 6.78 (s, 4 H, Cp) 6.67 (dd, 4 H, *J* = 6.5 Hz, *J* = 2.9 Hz, Ind-3,7) 1.49 (s 36 H, *t*-Bu). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 293 K): δ 151.7, 131.4, 130.0, 127.1, 126.2, 124.4, 122.9, 121.4, 105.0, 35.3, 31.6. C<sub>46</sub>H<sub>54</sub>Cl<sub>2</sub>Zr analysis found (calculated): C, 71.93 (71.84); H, 6.87 (6.87).

**Synthesis of Bis(2-(3,5-di-*tert*-butylphenyl)indenyl)-zirconium Dimethyl (4).** (2-(3,5-*t*-Bu<sub>2</sub>Ph)Ind)<sub>2</sub>ZrCl<sub>2</sub> (215 mg, 0.28 mmol) was suspended in 50 mL of diethyl ether and chilled to -78 °C in a dry ice/acetone bath. Methylolithium (1.4 M in Et<sub>2</sub>O, 0.44 mL, 0.62 mmol, 2.2 equiv) was added dropwise. The solution was stirred for 30 min at -78 °C, allowed to warm to room temperature, and stirred at room temperature for 4 h. The ether was removed in vacuo, and the remaining solid was extracted with toluene and filtered. The toluene was layered with pentane and placed in a -40 °C freezer. An off-white microcrystalline powder was obtained when the mother liquor was removed and was dried in vacuo to give 0.101 g of product (50%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz, 293 K): δ 7.65 (d, 4 H, *J* = 1.7 Hz, Ph-2,6) 7.57 (t, 2 H, *J* = 1.7 Hz, Ph-4) 6.93 (dd, 4 H, *J* = 6.5 Hz, *J* = 2.9 Hz, Ind-4,5) 6.77 (dd, 4 H, *J* = 6.5 Hz, *J* = 2.9 Hz, Ind-3,7) 6.45 (s, 4 H, Cp) 1.44 (s, 36 H, *t*-Bu) -0.76 (s, 6 H, Zr-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 293 K): δ 151.2, 132.6, 129.1, 124.6, 123.9, 122.1, 120.4, 98.1, 35.0, 32.3, 31.6. C<sub>48</sub>H<sub>60</sub>Zr analysis found (calculated): C, 79.08 (79.17); H, 8.38 (8.30).

**Acknowledgment.** Funding for this work was provided by BP Chemical Co. We thank Andy Ernst and Dave MacFarland of BP for catalyst synthesis and high-temperature GPC analysis, respectively. We thank Albemarle for the gift of boron activators. G.M.W. received a William R. and Sarah Hart Kimball Stanford Graduate Fellowship and S.L. a Veatch Memorial Fellowship, for which they are grateful.

## References and Notes

- Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.
- Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1346.
- Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Vols. 1, 2.
- Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267* (5195), 217–219.
- Hauptman, E.; Waymouth, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 11586–11587.
- Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174–11182.
- Lin, S.; Tagge, C. D.; Waymouth, R. M.; Nele, M.; Collins, S.; Pinto, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11275–11285.
- Petoff, J. L. M.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316–11322.
- Kravchenko, R.; Masood, A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 3635–3639.
- Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909–5916.
- Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707–2715.
- Wilmes, G. M.; Polse, J. L.; Waymouth, R. M. *Macromolecules*, in press.
- Lin, S.; Waymouth, R. M. *Acc. Chem. Res.*, in press.
- 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.
- Dreier, T.; Erker, G.; Froehlich, R.; Wibbeling, B. *Organometallics* **2000**, *19*, 4095–4103.
- Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelae, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348–4355.
- Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrel, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851–3858.
- Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000–1009.
- Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147–4155.
- Maiti, A.; Sierka, M.; Andzelm, J.; Golab, J.; Sauer, J. *J. Phys. Chem. A* **2000**, *104*, 10932–10938.
- Waymouth, R. M.; Kravchenko, R.; Bendig, L. L.; Moore, E. J.; Myers, C. L. US Patent 6,160,064, Dec 12, 2000.
- Ernst, A. P.; Moore, E. J.; Myers, C. L.; Quan, R. W. PCT Int. Appl. 0035975, 2000.
- Komen, C. M. D.; Bickelhaupt, F. *Synth. Commun.* **1996**, *26*, 1693–1697.
- Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908–6916.
- Hu, Y.; Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 3334–3340.
- Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024–9032.
- Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971–3977.
- Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. A: Chem.* **1998**, *128*, 53–64.
- Resconi, L. *J. Mol. Catal. A: Chem.* **1999**, *146*, 167–178.
- Brandow, C. G.; Mendiratta, A.; Bercaw, J. E. *Organometallics* **2001**, *20*, 4253–4261.
- Kaminsky, W.; Buschermohle, M. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Fontanille, M., Guyot, A., Eds.; Reidel: New York, 1987; pp 503–514.
- Kaminsky, W.; Buschermohle, M. U.S. Patent 4,841,004, 1989.
- Winter, A.; Antberg, M.; Rohrmann, J. U.S. Patent 4,962,248, 1990.
- Busico, V.; Cipullo, R.; Segre, A. L.; Talarico, G.; Vacatello, M.; Castelli, V. N. A. *Macromolecules* **2001**, *2001*, 8412–8415.
- Busico, V.; Cipullo, R.; Kretschmer, W. P.; Talarico, G.; Vacatello, M.; Van Axel Castelli, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 505–508.
- Nele, M.; Collins, S.; Dias, M. L.; Pinto, J. C.; Lin, S.; Waymouth, R. M. *Macromolecules* **2000**, *33*, 7249–7260.
- Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2001**, *123*, 1483–1489.
- Liu, Z. X.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 2915–2916.

MA012241C