Highly Isospecific Polymerization of Propylene with Bis(phenoxy-imine) Zr and Hf Complexes Using $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$ as a Cocatalyst

Aitha Vishwa Prasad, Haruyuki Makio, Junji Saito, Mitsuhiko Onda,[†] and Terunori Fujita*
R & D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura 299-0265
[†]*Mitsui Chemical Analysis & Consulting Service, Inc., 580-32 Nagaura, Sodegaura 299-0265*

(Received November 18, 2003; CL-031114)

Highly isospecific propylene polymerization was achieved by bis(phenoxy-imine) Zr and Hf complexes combined with $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$. Microstructural analyses of the isotactic polymers suggested that the polymerization probably proceeds via a site-control mechanism with a 1,2-insertion of propylene. Among the complexes examined, Hf complex **2** produced the highest tacticity polypropylene ([*mmmm*] 96.8%, T_m 165.1 °C) that is comparable to that made by the best heterogeneous Ziegler–Natta catalysts.

The development of homogeneous olefin polymerization catalysts based on well-defined coordination complexes has provided extraordinary opportunities to synthesize polymers with precisely controlled structures and to study polymerization pathways at the molecular level.[1] For example, new complexes have been prepared that allow highly stereospecific polymerization and a rational interpretation of the polymerization mechanisms. Although highly isospecific and syndiospecific propylene polymerizations have been achieved by explicitly designed molecular catalysts,[2] there is still considerable interest in the development of catalysts for the controlled polymerization of propylene due to the current importance and the great possibilities of polypropylenes (PPs). In particular, high stereoregularity of PPs is crucial for practical applications.

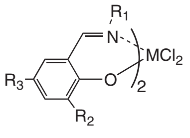
As disclosed in our patents[3] and in a series of subsequent papers,[4,5] we have developed bis(phenoxy-imine) early transition metal complexes (named FI Catalysts) for olefin polymerization, which display unique polymerization behavior. For instance, on activation with MAO, Ti–FI Catalysts can carry out highly syndiospecific, in some cases, living propylene polymerization via a chain-end control mechanism with an unusual 2,1 propylene insertion[5a,b] whereas Zr– and Hf–FI Catalysts polymerize propylene via a 1,2-insertion mechanism to afford atactic to slightly syndiotactic PPs.[5c] Conversely, in combination with $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$, Ti–FI Catalysts form ultra-high molecular weight atactic PPs while Zr– and Hf–FI Catalysts produce fairly isotactic PPs via a site-control mechanism.[5d] Therefore, propylene polymerization behavior of FI Catalysts has been a topic of great interest in recent years.[6,7] Herein, we describe ligand modifications that the isospecificity of Zr– and Hf–FI Catalysts to be dramatically enhanced from 55.7 to 96.9% of *mmmm* pentad.

Zr– and Hf–FI Catalysts **1–4** (Chart 1) were synthesized using a method similar to that described in our previous papers.[5b,d] Propylene polymerizations with **1–4** were investigated using $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$ as a cocatalyst at 25 °C under atmospheric pressure.[8] The polymerization results are summarized in Table 1. PPs obtained from FI Catalysts **1–4** appear visually to be mixtures, which consist of sticky amorphous and crystalline polymers. The GPC curves of these polymers display unimodal to multimodal molecular weight distributions, which are in stark contrast to sharp unimodal peaks of PPs arising from FI Catalysts **5** and **6**[5d] under the same conditions. In DSC studies, the polymers obtained show very high peak melting temperatures (T_m) of 154.9–164.8 °C, indicative of the formation of highly stereoregular polymers. We previously showed that the imine-functionality of FI Catalysts can be reduced by $^{i}Bu_3Al$ (and/or its contaminant $^{i}Bu_2AlH$) to amine-donors with concomitant formation of isobutene, leading to bis(pheonxy-amine) complexes having $^{i}Bu_2Al$ on the imine-nitrogen as a catalytically active species.[4b] The multimodal behavior observed for the present catalyst systems may be due to the incomplete reduction of the imine-functionality and/or the presence of several catalytically active species arising from the different binding geometries of the ligands.

Table 1. Propylene polymerization with FI Catalysts **1–6** using $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$ as a cocatalyst

FI Cat	Activity[a]	T_m/°C	$M_w/10^{-3}$[b]	M_w/M_n[b]
1	38	163.3	200	4.72[c]
2	62	164.8	530	14.6[c]
3	24.7	154.9	607	18.4[d]
4	638	160.1	1453	2.99
5[e]	94	103.5	209	2.42
6[e]	76	123.8	412	2.15

Conditions: reaction time, 20 min; temperature, 25 °C; toluene 250 mL; propylene, 0.1 MPa (100 L/h); complex, 0.005 mmol; $^{i}Bu_3Al$, 0.15 mmol; $Ph_3CB(C_6F_5)_4$, 0.01 mmol. [a]In kg/mol-M h. [b]Measured by GPC using polystyrene calibration. [c]Bimodal distribution. [d]Multimodal distribution. [e]See Ref. 5d.



1: M = Zr, R_1 = Cyclohexyl, R_2 = Adamantyl, R_3 = Methyl
2: M = Hf, R_1 = Cyclohexyl, R_2 = Adamantyl, R_3 = Methyl
3: M = Zr, R_1 = Phenyl, R_2 = Adamantyl, R_3 = Methyl
4: M = Hf, R_1 = Phenyl, R_2 = Adamantyl, R_3 = Methyl
5: M = Zr, R_1 = Phenyl, R_2 = t-Butyl, R_3 = H
6: M = Hf, R_1 = Phenyl, R_2 = t-Butyl, R_3 = H

Chart 1. FI Catalysts employed in propylene polymerization.

To obtain polymers in sufficient quantities for microstructural analyses, the catalyst concentration was doubled. The PPs obtained with complexes **1–4** (denoted as PP-**1–4**, hereafter) exhibit broad molecular weight distributions similar to those obtained with the lower catalysts concentration and can be divided into two portions by extraction with boiling hexane. The remaining crystalline polymers (hexane-insoluble parts: PP-**1**, 65 wt %; PP-**2**, 86 wt %; PP-**3**, 18 wt %; PP-**4**, 7 wt %) have relatively narrow molecular weight distributions (M_w/M_n: 2.1, M_w 172 × 10^3

for PP-**1**; 3.5, 346 × 10^3 for PP-**2**; 3.8, 1306 × 10^3 for PP-**3**; 4.7, 2554 × 10^3 for PP-**4**) and T_m of 154.9–165.1 °C. The ^{13}C NMR analyses of these hexane-insoluble stereoregular polymers from PP-**1** and PP-**2** revealed that FI Catalysts **1** and **2** afforded highly isotactic PPs whose isotacticities reached to [*mmmm*] 96.9% for PP-**1** and 96.8% for PP-**2** (Figure 1). The T_m (165.1 °C) and the isospecificity ([*mmmm*] 96.8%) obtained with Hf–FI Catalyst **2** represent some of the highest values for isotactic PPs ever synthesized.[2] The data in Table 1 suggest that the higher steric congestion near the polymerization center results in the formation of higher tacticity polymers. The integration of each pentad signal indicates that a site-control mechanism would be operative as is observed for PP-**5** and PP-**6** although deviations from the expected statistics are sometimes significant because of the small quantities of stereoirregular sequences which lead to poor signal-to-noise ratio.

To investigate chain-end structures, which may provide information on regiochemistry of chain propagation, low molecular weight polymer was synthesized with FI Catalyst **1** using H_2 as a chain transfer agent. Interestingly, highly isotactic polymer was selectively produced in this case probably because the other less stereospecific species were deactivated or transformed to highly stereospecific species in the presence of H_2. This result may provide insight into the structure of the desired active species and mechanism for this highly stereoselective reaction. The low M_w PP (M_w 17211, M_w/M_n 1.91) formed with $1/{}^{i}Bu_3Al/Ph_3CB(C_6F_5)_4/H_2$ contains three chain-end structures (^{13}C NMR analysis), i.e., *n*-propyl (46%), isobutyl (47%), and *n*-butyl (6%). Inversion structures, which were observed in the isotactic PP produced in the absence of H_2 (0.1%), could not be detected. Under the assumption that an occasional 2,1-insertion makes the subsequent monomer insertion slow and is followed exclusively by hydrogen chain transfer, it is concluded that 1,2-enchainment is the regular monomer insertion mode resulting in *n*-propyl and isobutyl groups as initiation and termination chain-ends, respectively, and *n*-butyl groups are termination chain-ends resulting from occasional regioerrors. Since the amount of inversion units of the PPs produced with Hf–FI Catalyst **2** (in the absence of H_2) was below the ^{13}C NMR detection level, we could not determine the insertion mode for **2** by this method. However, we assume that the propylene polymerization with **2** proceeds via a 1,2-insertion mechanism based on the similarity between Zr– and Hf–FI Catalysts.[5c,d]

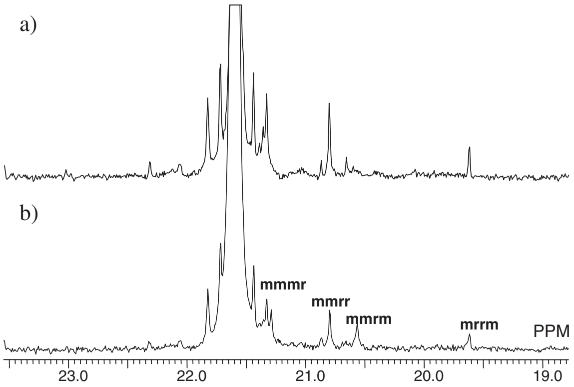


Figure 1. ^{13}C NMR spectra of the methyl pentad regions for the isotactic PPs: a) hexane insoluble part, PP-**1**; b) hexane insoluble part, PP-**2**.

In summary, we have demonstrated that highly isotactic PPs with extremely high T_ms (T_m 165.1 °C) can be produced by Zr– and Hf–FI Catalysts upon activation with $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$. These results are remarkable in view of the tremendous technological significance of high T_m isotactic PPs. The isospecific polymerization presumably proceeds via a site-control mechanism with 1,2-monomer enchainment. The susceptibility of the imine-functionality towards reduction by $^{i}Bu_3Al$ (and/or its contaminant $^{i}Bu_2AlH$) seems crucial to the high yield of highly isotactic PPs. The results presented herein together with our previous reports[3–5] indicate that FI Catalysts are capable of producing PP architectures ranging from atactic, highly syndiotactic to highly isotactic by the variation of the central metal, ligand structure and the cocatalyst.

Dr. M. Mullins is thanked for invaluable discussions and suggestions.

References

1 For reviews, see; a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34**, 1143 (1995). b) M. Bochmann, *J. Chem. Soc., Dalton Trans.*, **1996**, 255. c) G. J. P. Britovsek, V. C. Gibson, and D. F. Wass, *Angew. Chem., Int. Ed.*, **38**, 428 (1999). d) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, **103**, 283 (2003).

2 For reviews, see; a) G. W. Coates, *Chem. Rev.*, **100**, 1223 (2000). b) L. Resconi, L. Cavallo, A. Fait, and F. Piemontesi, *Chem. Rev.*, **100**, 1253 (2000).

3 For example, see; a) T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, and T. Tsutsui, EP 0874005 (1998), filing date: April 25, 1997. b) M. Mitani, Y. Yoshida, J. Mohri, K. Tsuru, S. Ishii, S. Kojoh, T. Matsugi, J. Saito, N. Matsukawa, S. Matsui, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, WO 01/55231 (2001), filing date: January 26, 2000.

4 For reviews, see; a) M. Mitani, T. Nakano, and T. Fujita, *Chem.—Eur. J.*, **9**, 2396 (2003). b) N. Matsukawa, S. Ishii, R. Furuyama, J. Saito, M. Mitani, H. Makio, H. Tanaka, and T. Fujita, *e-Polymers*, **2003**, no. 021 (http://www.e-Polymers.org). c) H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal.*, **344**, 477 (2002). d) Y. Nakayama, M. Mitani, H. Bando, and T. Fujita, *J. Synth. Org. Chem. Jpn.*, **61**, 1124 (2003).

5 a) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Tearo, T. Nakano, H. Tanaka, and T. Fujita, *J. Am. Chem. Soc.*, **125**, 4293 (2003) and references therein. b) R. Furuyama, J. Saito, S. Ishii, M. Mitani, S. Matsui, Y. Tohi, H. Makio, N. Matsukawa, H. Tanaka, and T. Fujita, *J. Mol. Catal. A*, **200**, 31 (2003). c) H. Makio, Y. Tohi, J. Saito, M. Onda, and T. Fujita, *Macromol. Rapid Commun.*, **24**, 894 (2003). d) J. Saito, M. Onda, S. Matsui, M. Mitani, R. Furuyama, H. Tanaka, and T. Fujita, *Macromol. Rapid Commun.*, **23**, 1118 (2002).

6 a) For a review, see; Y. Suzuki, H. Terao, and T. Fujita, *Bull. Chem. Soc. Jpn.*, **76**, 1493 (2003).

7 For recent examples, see; a) G. Milano, L. Cavallo, and G. Guerra, *J. Am. Chem. Soc.*, **124**, 13368 (2002). b) G. Talarico, V. Busico, and L. Cavallo, *J. Am. Chem. Soc.*, **125**, 7172 (2003). c) V. Busico, R. Cipullo, F. Cutillo, N. Friederichs, S. Ronca, and B. Wang, *J. Am. Chem. Soc.*, **125**, 12402 (2003). d) J. Tian, P. D. Hustad, and G. W. Coates, *J. Am. Chem. Soc.*, **124**, 3614 (2002). e) M. Lamberti, D. Pappalardo, A. Zambelli, and C. Pellecchia, *Macromolecules*, **35**, 658 (2002). f) G. W. Coates, J. Tian, and P. D. Hustad, US 6562930 (2003), filing date: September 18, 2001.

8 Propylene polymerization procedure: see Ref. 5d.

Published on the web (Advance View) January 26, 2004; DOI 10.1246/cl.2004.250