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COMMUNICATIONS

Fluorine- and Trimethylsilyl-Containing Phenoxy−Imine Ti Complex for Highly Syndiotactic Living Polypropylenes with Extremely High Melting Temperatures

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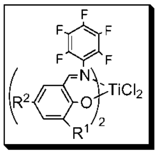
The developmental activities of catalysts capable of promoting stereospecific living propylene polymerization have been very intense. This is because these catalysts may provide potentially high-performance polymers such as monodisperse polypropylenes (PPs) with high melting temperatures (T_m's) and block copolymers containing the high T_m segments. Recent progress in the rational design of well-defined transition metal complexes for olefin polymerization[1] has spurred the development of high performance catalysts which initiate stereospecific living polymerization of α-olefins.[2] However, despite the fact that nearly perfect stereospecific propylene polymerization can be performed using group 4 metallocene catalysts, highly stereospecific living propylene polymerization has not yet been achieved.[3]

Previously, we found that a new series of titanium complexes bearing fluorine-containing phenoxy−imine chelate ligands (which are members of our FI Catalyst family) are capable of promoting living polymerization of ethylene or α-olefins or both to produce various block copolymers[4] and have described the details of their catalytic behavior[5] including unprecedented propylene polymerization mechanism.[5d] Recently, living propylene polymerization with fluorinated titanium FI Catalysts have been studied by Coates[6] and Zambelli.[7] Further efforts aimed at developing higher-performance FI Catalysts led us to the discovery of a new living propylene polymerization catalyst. In this communication, we introduce a Ti-FI Catalyst having fluorine- and trimethylsilyl-containing ligands, which polymerizes propylene above room temperature to form highly syndiotactic monodisperse PPs with extremely high T_m's.

The titanium complex employed in this study is bis[*N*-(3-trimethylsilylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]Ti(IV) dichloride (complex **1**, Figure 1). X-ray analysis indicates that complex **1** adopts a distorted octahedral structure with a *trans*-O, *cis*-N, and *cis*-Cl arrangement. Although the molecular structure is similar to that of complex **2** described in our previous paper,[5a] the bond distances of Ti−N and Ti−O are slightly elongated as a result of introducing a trimethylsilyl group into the ligand (Figure 2).

Polymerization of propylene with complex **1** using methylalumoxane (MAO) cocatalyst under atmospheric pressure at 25 °C for 5 h yielded crystalline polypropylene having an extremely narrow polydispersity ($M_n = 47\,000$, $M_w/M_n = 1.08$, Table 1, entry 3). The linear dependence of the M_n value upon the polymerization time (entries 2, 3) together with the narrow MWD values indicates that the polymerization proceeds in a living fashion under the given conditions.



1: R^1= $SiMe_3$, R^2= H
2: R^1= ^tBu, R^2= H
3: R^1= R^2= ^tBu
4: R^1= R^2= H

Figure 1. Fluorine-containing phenoxy-imine Ti complexes **1**−**4**.

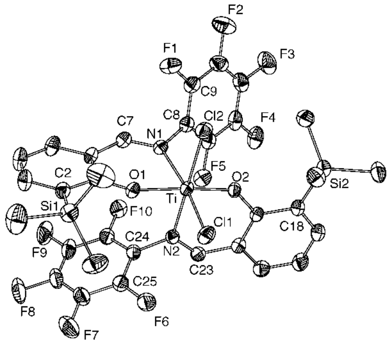


Figure 2. Molecular structure of complex **1** with thermal ellipsoids at 30% probability level. Selected bond distances (Å) and angles (deg): Ti−O(1) = 1.860(2), Ti−O(2) = 1.854(2), Ti−N(1) = 2.268(3), Ti−N(2) = 2.253(3), Ti−Cl(1) = 2.245(1), Ti−Cl(2) = 2.284(1), Si(1)−C(2) = 1.893(4), Si(2)−C(18) = 1.890(4), O(1)−Ti−O(2) = 165.6(1), N(1)−Ti−N(2) = 85.30(10) Cl(1)−Ti−Cl(2) = 99.19(4).

Table 1. Results of Propylene Polymerization with Complexes **1**−**4**/MAO[a]

entry	complex	T (°C)	time (h)	yield (g)	TOF[b] (h^{-1})	M_n[c] ($\times 10^3$)	M_w/M_n[c]	T_m[d] (°C)
1	**1**	0	5	0.151	72	24.7	1.08	156
2	**1**	25	3	0.205	162	34.2	1.05	153
3	**1**	25	5	0.293	139	47.0	1.08	152
4	**1**	50	3	0.157	124	25.5	1.18	150
5	**1**	50	5	0.237	112	35.1	1.23	149
6	**2**	0	5	0.144	68	23.6	1.05	136
7	**2**	25	5	0.183	87	28.5	1.11	137
8	**2**	50	5	0.151	72	18.6	1.59	117
9	**3**	0	5	0.109	52	19.2	1.05	141
10	**3**	25	5	0.219	104	29.8	1.15	135
11	**3**	50	5	0.263	125	31.3	3.19	127
12	**4**	25	5	1.534	729	189.0	1.51	n.d.[e]

[a] Conditions: complex (10 μmol), cocat. MAO (2.5 mmol), 1 atm, toluene 250 mL. [b] Turnover frequency. [c] Determined by GPC using polypropylene calibration. [d] Melting temperature of produced PP determined by DSC. [e] Not detected.

Microstructural analysis using ^{13}C NMR spectroscopy reveals that the monodisperse polymer is highly syndiotactic PP (syn-PP) containing 93% rr triad. The isolated m-dyad errors suggest that the polymer is probably produced via a chain-end control mechanism.[8] Interestingly, the syn-PP produced by **1** displays an extremely high T_m (152 °C). Moreover, polymerization at 0 °C

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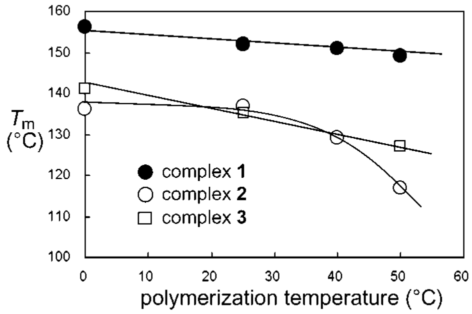

Figure 3. Plots of T_m vs polymerization temperature with **1**−**3**/MAO.

afforded syn-PP with an exceptionally high T_m of 156 °C ([rr] 94%), which probably represents the highest value reported to date for not only monodisperse syn-PPs but also highly syn-PPs obtained with exquisitely designed group 4 metallocene catalysts.[9,10] On the other hand, complexes **2**[4,5] and **3**[6] previously introduced as catalysts for highly syndiospecific living propylene polymerization, provided lower tacticity polymers with much lower T_m's (135−141 °C, Table 1, entries 6, 7, 9, 10). These results show that complex **1** possesses a great potential for syndiospecific living propylene polymerization.

Surprisingly, at 50 °C, complex **1** initiated living propylene polymerization and furnished narrow polydispersity syn-PPs with very high T_m's (150, 149 °C, Table 1, entries 4 and 5 and Figure 3), which is of great significance because generally chain-end control rapidly loses stereoregulating ability at elevated temperatures.

In contrast, at 50 °C, complexes **2** and **3** produced syn-PPs having T_m's below 130 °C (Table 1, entries 8 and11 and Figure 3), with broadened polydispersities (M_w/M_n; **2**, 1.59; **3**, 3.19). These results indicate that the R^1 substituent has an effect on syndiospecificity of fluorinated Ti-FI Catalysts.

To gain further information on the effect of R^1 substituent, we synthesized complex **4** having a hydrogen atom at R^1 position and investigated its potential as a propylene polymerization catalyst. Complex **4** showed considerably higher activity than **2** and **3**, probably due to the structurally open nature of the complex (entry 12), and much lower syndiospecificity (rr 43%, no T_m). These results suggest that the steric bulk of the R^1 substituent plays a key role in determining the syndiospecificity of the polymerization. Although, at present, mechanistic details for propylene polymerization with fluorinated FI Catalysts are not clear, it is obvious that the ligand structure of the catalyst has a dramatic effect on polymerization behavior and that sterically bulky substituents at the R^1 position result in a highly controlled syndiospecific polymerization though chain-end control. Therefore, we have given the name "ligand-directed chain-end control" to our newly discovered highly controlled syndiospecific propylene polymerization that enables us to have highly syn-PPs with extremely high T_m's. In summary, a new titanium complex with fluorine- and trimethylsilyl-containing phenoxy−imine chelate ligands has been introduced, which forms highly syndiotactic monodisperse PPs with high T_m's even at elevated temperatures. The results described herein along with our previous reports[11] suggest that FI Catalysts are capable of producing novel polymers that are unobtainable from conventional Ziegler−Natta catalysis.

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Supporting Information Available: Synthesis and characterization of the complexes, polymer synthesis, and analysis data (GPC, DSC, NMR) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kaminsky, W. *Catal. Today* **1994**, *20*, 257−271. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(2) (a) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009. (b) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665. (c) Liang, L. C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797−5798. (d) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706−10707. (e) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959.

(3) (a) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 2896−2900. (b) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142−3145.

(4) Mitani, M.; Yoshida, Y.; Mohri, J.; Tsuru, K.; Ishii, S.; Kojoh, S.; Matsugi, T.; Saito, J.; Matsukawa, N.; Matsui, S.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. WO Pat. 01/55231 A1, 2001; *Chem. Abstr.* **2001**, *135*, 137852.

(5) (a) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2918−2920. (b) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576−577. (c) Kojoh, S.; Matsugi, T.; Saito, J.; Mitani, M.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 822−823. (d) Saito, J.; Mitani, M.; Onda, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Nakano, T.; Tanaka, H.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2001**, *22*, 1072−1075. (e) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, 124, 3327−3336.

(6) (a) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134−5135. (b) Hustad, P. D.; Tian, J.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, 124, 3614−3621.

(7) Lamberti, M.; Pappalardo, D.; Zambelli, A.; Pellecchia, C. *Macromolecules* **2002**, *35*, 658−663.

(8) This mechanism is also operative in propylene polymerization with complexes **2** and **3**. See refs 5b and d, 6, and 7.

(9) (a) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573. (b) Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A. *J. Mol. Catal. A: Chem.* **1999**, *140*, 225−233.

(10) Obviously, the T_m's of monodisperse syn-PPs arising from fluorinated FI Catalysts are higher than the values expected from the syndiotacticity of the polymers. (For example; syn-PP formed with $Ph_2C(Cp, 2,7\text{-di-}t\text{-Bu-Flu})ZrCl_2$, [rr] 95%, T_m 148 °C; under the same DSC measurement conditions. Shiomura, T.; Kohno, M.; Inoue, N.; Yokote, Y.; Akiyama, M.; Asanuma, T.; Sugimoto, R.; Kimura, S.; Abe, M. *Catalyst Design for Tailor-Made Polyolefins*; Kodansha and Elsevier: Tokyo and Amsterdam, 1994; pp 327−338). The difference probably originates from the microstructures or unimodality of the polymers. Detailed investigations are underway.

(11) (a) Fujita, T.; Tohi, Y.; Mitani, M.; Matsui, S.; Saito, J.; Nitabaru, M.; Sugi, K.; Makio, H.; Tsutsui, T. Eur. Patent, EP-0874005, 1998; *Chem. Abstr.* **1998**, *129*, 331166. (b) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847−6856. (c) Saito, J.; Mitani, M.; Matsui, S.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2000**, *21*, 1333−1336. (d) Ishii, S.; Saito, J.; Mitani, M.; Mohri, J.; Matsukawa, N.; Tohi, Y.; Matsui, S.; Kashiwa, N.; Fujita, T. *J. Mol. Catal. A* **2002**, *179*, 11−16.

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