Highly Syndiospecific Living Polymerization of Propylene Using a Titanium Complex Having Two Phenoxy-Imine Chelate Ligands

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A titanium complex having fluorine-containing phenoxy-imine chelate ligands, when activated with methylalumoxane (MAO), promotes a highly stereospecific living polymerization of propylene at room temperature to produce syndiotactic polypropylene (rr = 87%, T_m = 137 °C) having extremely narrow polydispersity (M_w/M_n = 1.11).

Living olefin polymerizations can be used for the preparation of precisely-controlled polymers, such as monodisperse polymers, terminally functionalized polymers, and block copolymers, and have been one of the most challenging subjects of both fundamental and practical interest. Accordingly, there has been intensive research on well-defined transition metal complexes with a view towards developing high performance catalysts for the living polymerization of olefins. A number of intriguing catalysts for the living polymerization of both ethylene and α-olefins have been reported thus far.[1] Nevertheless, highly stereospecific living polymerization of propylene has not yet been achieved despite the achievement of nearly perfect stereospecific polymerization of propylene using group 4 metallocene catalysts.[2] Previously, we found that group 4 transition metal complexes bearing two phenoxy-imine chelate ligands, named FI Catalysts, display high ethylene polymerization activities.[3] Subsequent studies performed by us[4] and other groups[5] have shown that FI Catalysts exhibit high catalytic performance for the polymerization of not only ethylene but also ethylene-propylene, propylene and 1-hexene. Recently, we have demonstrated that a titanium complex with fluorine-containing phenoxy-imine chelate ligands behaved as an excellent catalyst for living ethylene polymerization to provide high molecular weight polyethylenes having extremely narrow polydispersities.[6] Further research has revealed that the titanium complex promotes highly syndiospecific living polymerization of propylene at room temperature to produce monodisperse syndiotactic polypropylene. Thus, in this communication, we would like to describe the catalytic performance of the titanium complex for the living polymerization of propylene.

The titanium complex employed in this study is bis[*N*-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (complex **1**, Figure 1). The complex **1** was prepared in 67 % yield by the treatment of $TiCl_4$ with 2 equiv of the lithium salt of *N*-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline, prepared by the Schiff-base condensation of 3-*t*-butylsalicylaldehyde with 2,3,4,5,6-pentafluoroaniline in 98% yield, in diethyl ether.[6,7]

Polymerization of propylene with complex **1** using methylalumoxane (MAO) under atmospheric pressure at 25 °C for 5 h yielded crystalline polypropylene, M_n = 28500, having an extremely narrow polydispersity, M_w/M_n = 1.11, with 3.7 kg-polymer/mol-cat·h of activity (Table 1, entry 1). The M_w/M_n value suggests that complex **1** /MAO catalyst system may have the character of living polymerization.

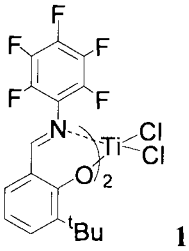

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Figure 1. Bis[*N*-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoro anilinato]titanium(IV) dichloride (**1**).

Table1. Propylene polymerization results with complex **1**/MAO

Entry	Time / h	Yield / mg	Activity[a]	M_n[b] / 10^4	M_w/M_n
1[c]	5	183	3.7	2.85	1.11
2[d]	1	158	15.8	3.09	1.07
3[d]	2	312	15.6	5.28	1.10
4[d]	3	460	15.3	7.38	1.10
5[d]	5	713	14.3	10.8	1.14

Conditions: 25 °C, Complex; 10 μmol. Cocatalyst; MAO (purchased from Albemale); 2.5 mmol. [a]/kg-polymer·mol-cat^{-1}·h^{-1}. [b]M_n values were determined by using polypropylene calibration. [c]0.1 MPa pressure, toluene 250 mL. [d]0.6 MPa pressure, toluene 380 mL.

To examine whether the polymerization is living or not, M_n and M_w/M_n values of the polymerization conducted under 0.6 MPa of propylene at 25 °C were monitored as a function of polymerization time (Figure 2). The linear dependence of the M_n value upon the polymerization time (entries 2 – 5) together with the narrow M_w/M_n values for all entries, M_w/M_n = 1.07 – 1.14, indicates that the polymerization is indeed living.[8]

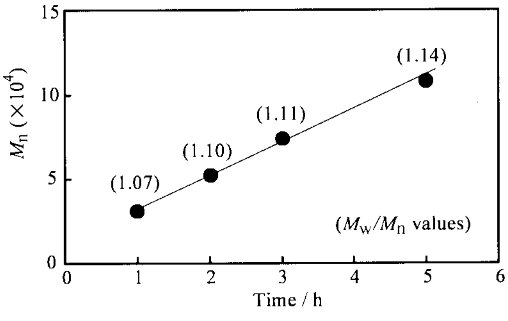

Figure 2. Plot of M_n values as a function of polymerization time for the polymerization of propylene; (Table 1, entries 2–5)

Initiation efficiencies for the polymerization lie in the range of 51–66%. To the best of our knowledge, this is the first example of a room-temperature living polymerization of propylene.

The polypropylene produced by complex **1**/MAO under atmospheric pressure (Table 1, entry 1) displays a peak melting temperature (T_m) of 137 °C, indicative of a high degree of stereocontrol. Microstructural analysis of this living polypropylene using ^{13}C NMR spectroscopy revealed that the polypropylene is syndiotactic. Thus, the methyl triad region of the ^{13}C NMR spectrum of the polypropylene contains 87% rr triads. As far as we are aware, the rr triad represents the highest reported to date for monodisperse syndiotactic polypropylenes. The syndiotactic polypropylene possesses isolated m-dyad errors (>10%) in the methyl pentad region, suggesting that the syndiospecific polymerization proceeds via a chain-end control mechanism. A possible explanation for this very high syndiotacticity derived from the chain-end control is that a fluorine in the ligand interacts with a polymer chain to fix a polymer conformation near the polymerization reaction center, resulting in the enhancement of the chain-end control.[9] Surprisingly, syndiotactic polypropylene (M_n = 2000, M_w/M_n = 1.08), obtained from complex **1**/MAO under atmospheric pressure at 25 °C for 15 min, possesses 98% rr triads (Figure 3).[9] This polypropylene is the most stereoregular syndiotactic polypropylene produced by non-metallocene catalysts. Detailed mechanistic studies together with the analysis of polymer structures are underway.

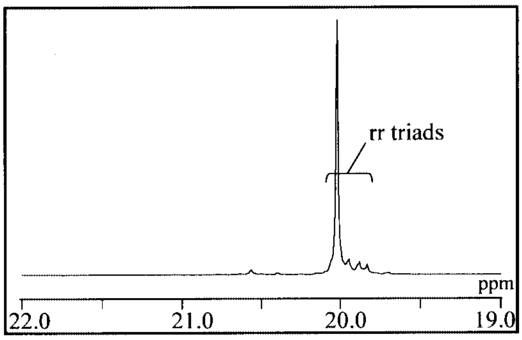

Figure 3. The ^{13}C NMR spectrum of the methyl triad region of the syndiotactic polypropylene produced under atmospheric pressure (M_n = 2000).

In summary, a high performance catalyst has been introduced for the living polymerization of propylene leading to highly syndiotactic polypropylene with extremely narrow polydispersity. The results presented herein together with our previous results of the living ethylene polymerization using the same catalyst system provide a new method for creating monodisperse polymers, terminally functionalized polymers and block copolymers, all of which are anticipated to possess novel properties and uses as high performance polymers.

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7 Complex **1**: $TiC_{34}H_{26}N_2O_2F_{10}Cl_2\cdot 1/3Et_2O$, ^1H NMR (270 MHz, $CDCl_3$, TMS): δ 1.35 (s, 18 H, *t*Bu), 7.02 (t, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 2H), 8.22 (s, 2 H, CH=N), 1.21 (t, *J* = 7.0 Hz,$(CH_3C\underline{H}_2)O$), 3.48 (q, *J* = 7.0 Hz,$(C\underline{H}_3CH_2)O$),; Anal. Calcd for $TiC_{34}H_{26}N_2O_2F_{10}Cl_2\cdot 1/3Et_2O$: C, 51.25; H, 3.57; N, 3.38; F, 22.95; Cl, 8.52; Ti, 5.78 %. Found: C, 51.71; H, 4.04; N, 3.79; F, 21.68; Cl, 8.92; Ti, 5.40 %. FD-mass, *m/z* 802 (M^+: $TiC_{34}H_{26}N_2O_2\ F_{10}Cl_2$).

8 The results of entry 5 suggest that catalyst deactivation is not negligible for 5-h polymerization.

9 Preliminary DFT calculations suggest that a fluorine adjacent to the imine-nitrogen strongly interacts with a β-hydrogen of a polymer chain, leading to the fixation of the polymer conformation near the polymerization reaction center. This interaction may be responsible for the realization of both the room-temperature living polymerization and the high stereospecificity by complex **1**/ MAO. Detailed calculation results will be reported shortly.