New Titanium Complexes Having Two Indolide-Imine Chelate Ligands for Living Ethylene Polymerization

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Three new titanium complexes having two indolide-imine ligands were synthesized and investigated as ethylene polymerization catalysts. These complexes using MAO as a cocatalyst promoted ethylene polymerization at 25 °C to produce polyethylenes (M_n:11000–41800) having narrow molecular weight distributions (M_w/M_n: 1.11–1.14), displaying very high activities (52–288 kg-PE/mol-Ti·h·atm).

The development of high performance living olefin polymerization catalysts has been the subject of extensive study for many years since living olefin polymerization is a powerful tool for creating precisely-controlled polymers such as monodisperse polymers, end-functionalized polymers, and block copolymers.[1,3k] The living olefin polymerization requires low temperatures to suppress the side reactions, namely chain termination or transfer reactions and, thus, it generally produces a relatively low molecular weight polymer, displaying low activity. Much research effort devoted to the study on soluble, well-defined transition metal complexes for olefin polymerization[2] has resulted in the introduction of a variety of living olefin polymerization catalysts working at relatively high temperatures. There are, however, a limited number of examples of room-temperature living ethylene polymerizations using soluble, well-defined transition metal complexes so far.[1f,1g,1o]

Recently, we have found, as a result of ligand-oriented catalyst design research, that transition metal complexes having non-symmetric bidentate ligand(s) (e.g., phenoxy-imine ligand, pyrrolide-imine ligand, and imine-pyridine ligand) exhibit high catalytic performance for olefin polymerization.[3] These results inspired us to conduct further study on transition metal complexes having non-symmetric bidentate ligand(s) as potentially viable olefin polymerization catalysts.

In this paper, we introduce three titanium complexes, bearing two indolide-imine chelate ligands, which promote living ethylene polymerization at room temperature.

A general synthetic route for titanium complexes employed in this study is shown in Scheme 1. The indolide-imine ligands of general structures **A**–**C**, namely 7-(*N*-aryliminomethyl) indole ligands, are prepared in high yields (**A**: 98%, **B**: 64%, **C**: 72%) by the Schiff-base condensation of the desired primary amine with 7-formylindole.[4] The titanium complexes possessing two indolide-imine ligands, namely bis[7-(*N*-aryliminomethyl)indolinyl]titanium(IV) dichloride complexes, are obtained as dark purple powder in moderate yields (**1**: 36%, **2**: 27%, **3**: 29%) by the treatment of $TiCl_4$ with 2 equiv of the lithium salt of the indolide-imine ligand.[5]

Complexes **1**–**3** were investigated as ethylene polymerization catalysts using MAO as a cocatalyst for 10 min at 25 °C under atmospheric pressure.[6] The results are collected in Table 1.

Scheme 1.

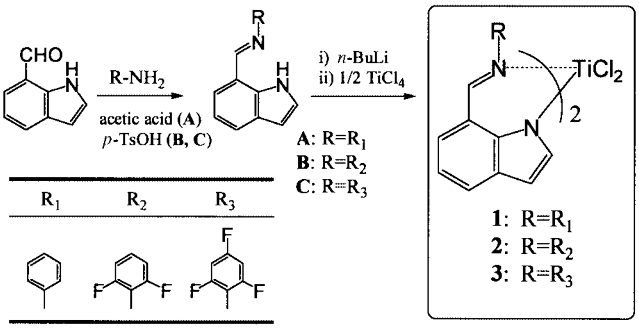

Table 1. Ethylene polymerization results using complexes **1–3** / MAO catalyst systems

Entry	Complex	Yield /g	Activity [b]	M_n[c] /10^4	M_w/M_n[c]	[d] %
1	**1**	0.043	52	1.21	1.14	71
2	**2**	0.050	60	1.10	1.13	91
3	**3**	0.240	288	4.18	1.11	115
4[a]	**3**	0.242	290	5.32	1.24	91

Conditions: 25 °C, 0.1 MPa pressure, toluene; 250 mL, polymerization time; 10 min, ethylene; 100 L/h, [complex]=0.02 mM, MAO (Albemarle); [Al]=5.0 mM, [a]50 °C. [b]/kg-PE·mol-Ti^{-1}·h^{-1}·atm^{-1}. [c]M_w, M_n values; GPC analysis. [d]Initiation efficiency for the polymerization.

The activities obtained were in the range of 52–288 kg-PE/mol-Ti·h·atm. In all cases, solid polyethylene was obtained. The melting temperature (T_m) of the polyethylenes, based on DSC measurement, lies in the range of 132.2–134.2 °C, suggesting that the polyethylenes possess a linear structure. GPC analyses revealed that the polyethylenes produced at 25 °C possess narrow molecular weight distributions (M_w/M_n: 1.11–1.14, entries 1–3) for their high molecular weights (M_n: 11000–41800). The M_w/M_n values suggest that complexes **1**–**3** / MAO catalyst systems have the character of living polymerization. Initiation efficiencies for the polymerization are more than 71%.[7] Interestingly, ethylene polymerization using complex **3** / MAO at 50 °C for 10 min produced polyethylene having a reasonably narrow molecular weight distribution (M_w/M_n: 1.24, M_n: 53200), displaying higher catalytic activity (290 kg-PE/mol-Ti·h·atm) (entry 4). A comparison of the polymerization results of entries 1–3 indicates that the substituents on the imine nitrogen influenced catalytic activities. The introduction of fluorine atoms to the benzene ring on imine nitrogen is supposed to enhance the electrophilicity of the titanium metal in active species for olefin polymerization. Thus, concerning the titanium complexes we studied, the electrophilicity of the titanium metal in active species probably plays a predominant role in determining the polymerization activity. The highest activity (288 kg-PE/mol-Ti·h·atm) (entry 3) is extremely high through the polymerization proceeded in a living fashion.

Catalytic performance of complex **3** / MAO catalyst system was further investigated since this catalyst system exhibited the highest catalytic activity and the narrowest molecular weight value. M_n and M_w/M_n values of complex **3** / MAO were monitored as a function of polymer yield at 25 °C. As shown in Figure 1, the M_n value increased proportionally with the polymer yield while the narrow M_w/M_n value was retained, further confirming a living polymerization.

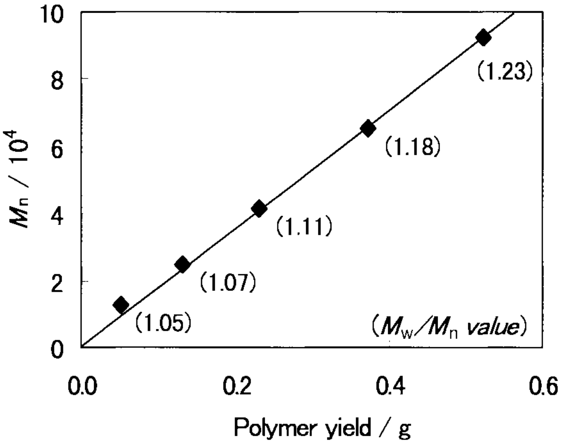

Figure 1. Plot of M_n and M_w/M_n as a function of polymer yield for the polymerization of ethylene; complex **3** / MAO.

Conditions: 25 °C, 0.1 MPa pressure, toluene; 250 mL, ethylene; 100 L/h, [**3**] = 0.02 mM, MAO (Albemarle); [Al] = 5.0mM, M_w, M_n values; GPC analysis.

In summary, three new titanium complexes with two indolide-imine chelate ligands were prepared and found to be room-temperature living ethylene polymerization catalysts. The influence of substitution groups of the ligands and cocatalysts as well as potential applications of the catalyst systems are under active investigation.

References and notes

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5 Complex **1**: ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS); δ 6.01 (d, 2H), 6.7–7.3 (m, 4H(indole-H) + 10H(phenyl-H)), 7.55 (d, 2H), 8.24 (s, 2H), 8.35 (d,2H). Anal. Calcd for $C_{30}H_{22}N_4Cl_2Ti$: C, 64.66. H, 3.98; N, 10.05%. Found: C, 64.18. H, 4.10; N, 10.21%. FD-mass: *m/z*: 556(M^+). Complex **2**: ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS); δ 5.98 (d, 2H), 6.14 (m, 2H), 6.74 (d, 2H), 6.77 (d, 2H), 7.10 (t, 2H), 7.31 (m, 2H), 7.65 (m, 2H), 8.18 (m, 2H), 8.31 (s, 2H). FD-mass: *m/z*: 628(M^+). Reasonable elemental analysis data were not obtained since complex **2** was unstable and decomposed on standing. Complex **3**: ^{1}H NMR (270MHz, $CDCl_3$, 25 °C, TMS); δ 5.98 (m, 2H), 6.08 (d, 2H), 6.51 (m, 2H), 7.14 (t, 2H), 7.33 (m, 2H), 7.73 (m, 2H), 8.20 (m, 2H), 8.29 (s, 2H). Anal. Calcd for $C_{30}H_{16}N_4$ F_6Cl_2Ti: C, 54.17. H, 2.42; N, 8.42%. Found: C, 54.15. H, 2.09; N, 8.23%. FD-mass: *m/z*: 664(M^+).

6 General polymerization procedure: Flow of ethylene gas (100 L/h) was charged into 250 mL of toluene at 25 °C. To this solution, MAO (Albemarle MAO, 1.2 M toluene solution) and a toluene solution of a complex was added at the desired polymerization temperature. After the prescribed time, 25 mL of isobutyl alcohol was added to terminate the polymerization.

7 Although initiation efficiency cannot be discussed accurately for such low polymer yields, the values suggest the high efficiency for generating active species.