Living Polymerization of Ethylene with a Titanium Complex Containing Two Phenoxy-Imine Chelate Ligands

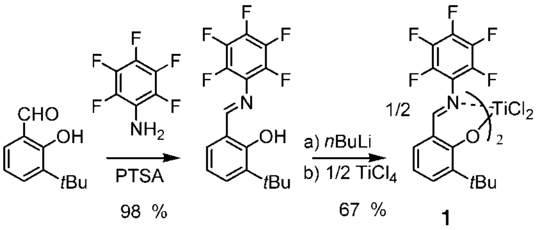
Junji Saito, Makoto Mitani, Jun-ichi Mohri,
Yasunori Yoshida, Shigekazu Matsui, Sei-ichi Ishii,
Shin-ichi Kojoh, Norio Kashiwa, and Terunori Fujita*

Dedicated to Dr. Kenji Saeki
on the occasion of his 60th birthday

Living polymerization of olefins is of great importance in the preparation of precisely controlled polymers such as monodisperse polymers, terminally functionalized polymers, and block copolymers, all of which are expected to display novel physical properties. Recent advances in the design and synthesis of well-defined transition metal complexes for olefin polymerization[1] have enabled the realization of living polymerization of various olefins.[2] On paper, living polymerization of an olefin providing high activity with high molecular weight value at high temperatures is feasible by controlling chain termination or transfer steps (e.g., β-hydride elimination, β-alkyl elimination, and chain transfer to a cocatalyst). However, the living polymerization of olefins is performed at low temperatures, normally below room temperature, to suppress these processes. Thus, it generally exhibits low activity with insufficient molecular weight value, highly restricting application to the preparation of the desired polymers.

We have acquired Group 4 transition metal complexes bearing two phenoxy-imine chelate ligands, named FI catalysts, which display high catalytic performance for the polymerization of ethylene, ethylene-propylene, or 1-hexene.[3] In the course of our studies on FI catalysts having one or more heteroatoms and/or heteroatom-containing substituents in the ligands, we found a fluorine-containing titanium FI catalyst that exhibits unprecedented catalytic performance for the polymerization of ethylene. Here we describe the highly active living polymerization of ethylene catalyzed by a titanium FI catalyst, creating high molecular weight polyethylene with a narrow polydispersity at high polymerization temperatures.

The fluorine-containing phenoxy-imine ligand employed in this study is *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline. The ligand was prepared in 98% yield by the Schiff base condensation of 2,3,4,5,6-pentafluoroaniline with 3-*tert*-butylsalicylaldehyde in toluene using *p*-toluenesulfonic acid (PTSA) as a catalyst. Complex **1** was obtained as a brown powder in 67% yield by treatment of $TiCl_4$ with two equivalents of the lithium salt of *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline in diethyl ether according to Scheme 1.



Scheme 1. Synthetic route to compound **1**. PTSA = *p*-toluenesulfonic acid.

Single crystals of complex **1** suitable for an X-ray structure determination were grown from a saturated solution in pentane/CH_2Cl_2. The structure features a distorted octahedral complex in which the titanium atom is bound to two *cis*-coordinated phenoxy-imine [O,N] chelating ligands (the oxygen atoms are situated in *trans* position, O-Ti-O 163.6°) and the two chlorine atoms (in *cis* position, Cl-Ti-Cl 96.4°; Figure 1).[4] Under the assumption that two chlorine-bound sites are transformed into olefin polymerization sites while retaining their *cis* relationship, an active species originating from complex **1** would have two *cis* sites for efficient olefin polymerization.

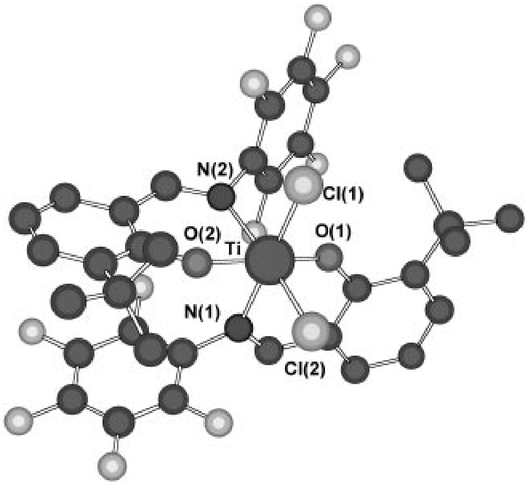


Figure 1. X-ray structure of **1**. Hydrogen atoms and a CH_2Cl_2 molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–O(1) 1.841(3), Ti–O(2) 1.841(3), Ti–N(1) 2.240(4), Ti–N(2) 2.219(4), Ti–Cl(1) 2.289(2), Ti–Cl(2) 2.261(2); O(1)-Ti-O(2) 163.6(1), N(1)-Ti-N(2) 87.2(1) Cl(1)-Ti-Cl(2) 96.42(6).

Ethylene polymerizations were performed at 25 °C under atmospheric pressure for one minute with complex **1** and, for comparison, $[Cp_2ZrCl_2]$ and $[Cp_2TiCl_2]$ using methylalumoxane (MAO) as a cocatalyst. The results are presented in Table 1. Complex **1** proved to be competitive with the metallocenes in terms of catalytic activity. Thus, complex **1** displayed a very high turnover frequency (TOF) of $20000\,min^{-1}atm^{-1}$ (entry 1), which was comparable to those exhibited by $[Cp_2ZrCl_2]$ ($18600\,min^{-1}atm^{-1}$, entry 2) and $[Cp_2TiCl_2]$ ($30500\,min^{-1}atm^{-1}$, entry 3) under the same polymerization conditions. The melting temperature (T_m) of the produced polyethylene (entry 1) was 135.2 °C. The ^{13}C NMR analysis of the polymer indicates that the polyethylene has a linear structure with virtually no branching. The polyethylene produced with complex **1** possesses a narrow polydispersity

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[*] Dr. T. Fujita, J. Saito, Dr. M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, Dr. S. Kojoh, Dr. N. Kashiwa
R&D Center, Mitsui Chemicals, Inc.
580-32 Nagaura, Sodegaura-City
Chiba 299-0265 (Japan)
Fax: (+81) 438-64-2375
E-mail: terunori.fujita@mitsui-chem.co.jp

Table 1. Results of ethylene polymerization using complex **1**, [Cp_2ZrCl_2], or [Cp_2TiCl_2].[a]

Entry	Complex	Yield [g]	TOF [$min^{-1}atm^{-1}$]	M_n [$\times 10^3$]	M_w/M_n	T_m [°C]
1	**1**	0.28	20000	412	1.13	135.2
2	[Cp_2ZrCl_2]	0.26	18600	157	1.73	133.4
3	[Cp_2TiCl_2]	0.43	30500	309	1.97	134.9

[a] Conditions: ethylene, atmospheric pressure (1667 mL min^{-1}), toluene (250 mL), 25 °C, 1.0 min, catalyst (0.5 µmol), cocatalyst MAO (1.25 mmol, purchased from Albemarle).

($M_w/M_n = 1.13$), which suggests a living polymerization. The molecular weight ($M_n = 412000$) represents one of the highest values and the TOF of 20000 min^{-1}atm^{-1} is one of the highest activities reported to date with regard to living ethylene polymerizations.

To further confirm the living polymerization, the M_n and M_w/M_n values of the polymerizations using diluted ethylene with nitrogen under atmospheric pressure at 25 °C were monitored as a function of polymerization time. A linear relationship between M_n and polymerization time as well as a narrow range of M_w/M_n values (1.05–1.13) were found for all runs, indicating a living polymerization (Figure 2a).[5] To the best of our knowledge, this is the first example of an exceptionally high speed, room-temperature living ethylene polymerization which produces very high molecular weight polyethylene with a narrow polydispersity ($M_w/M_n < 1.20$).[6]

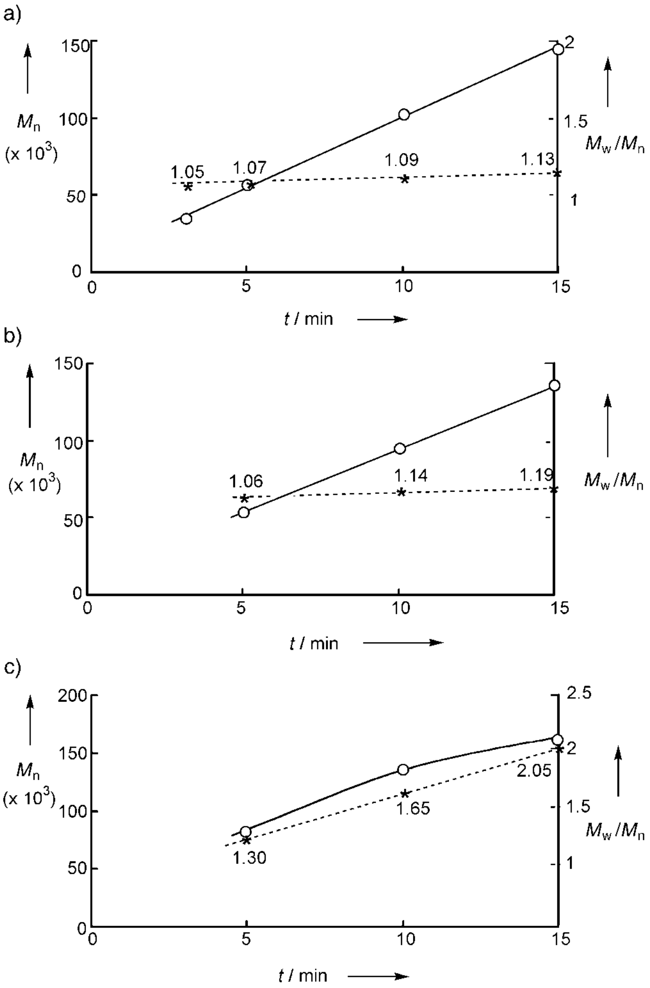

Figure 2. Plots of M_n and M_w/M_n as a function of polymerization time t for ethylene polymerization at a) 25 °C, b) 50 °C, and c) 75 °C using diluted ethylene (33 mL h^{-1} for a, b; 83 mL h^{-1} for c) with nitrogen (833 mL h^{-1}; **1**: 1 µmol, MAO: 1.25 mmol). ○: M_n, *: M_w/M_n.

Surprisingly, there is practically no chain termination or transfer step in the complex **1**/MAO system for at least 30 min, even in the absence of ethylene, indicating the high potential of the system for living ethylene polymerizations (Table 2). Thus, treatment of the complex **1**/MAO with ethylene-saturated toluene at room temperature under a nitrogen atmosphere for 35 min—the ethylene was substantially consumed within 5 min as indicated by entries 1 and 2—and subsequent ethylene gas feed (333 mL min^{-1}, 2 min) to the resulting mixture resulted in the formation of polyethylene having a narrow polydispersity ($M_w/M_n = 1.17$).

Table 2. Results of ethylene polymerization with complex **1** using ethylene-saturated toluene under N_2 or N_2 followed by ethylene feed.[a]

Entry	Conditions	Yield [g]	M_n [$\times 10^3$]	M_w/M_n
1	5 min under N_2	0.800	65.8	1.10
2	35 min under N_2	0.775	73.0	1.12
3	1. 35 min under N_2 2. 2 min with ethylene[b]	1.317	98.6	1.17

[a] Conditions: toluene (250 mL, saturated with ethylene), complex (10 µmol), cocatalyst MAO (2.5 mmol). [b] Ethylene (333 mL min^{-1}).

To investigate the living nature of the complex **1**/MAO catalyst system, ethylene polymerizations were carried out at higher temperatures (50, 75, and 90 °C). As summarized in Table 3, complex **1** was capable of producing polyethylenes having narrow polydispersities (M_w/M_n 1.08–1.15) at 50 and 75 °C.

Table 3. Results of ethylene polymerization with complex **1** at various temperatures.[a]

Entry	**1** [µmol]	T [°C]	t [min]	Yield [g]	TOF [$min^{-1}atm^{-1}$]	M_n [$\times 10^3$]	M_w/M_n
1	0.5	50	0.5	0.17	24300	257	1.08
2	0.5	50	1.0	0.30	21400	424	1.13
3	1.0	75	0.5	0.25	17900	214	1.09
4	1.0	75	1.0	0.45	16100	329	1.15
5	2.0	90	0.5	0.20	7140	102	1.22
6	2.0	90	1.0	0.46	8210	167	1.30

[a] Conditions: ethylene, atmospheric pressure (1667 mL min^{-1}), toluene (250 mL), cocatalyst MAO (1.25 mmol, purchased from Albemarle).

The M_n and M_w/M_n values of the polymerizations at 50 and 75 °C using diluted ethylene with nitrogen under atmospheric pressure were monitored as a function of polymerization time. At 50 °C a linear relationship between M_n and polymerization time as well as narrow M_w/M_n values were found for all runs ($M_w/M_n = 1.06$–1.19, Figure 2b). Moreover, at 75 °C, though chain termination or transfer and/or catalyst deactivation occurred, complex **1** still possessed some characteristics of living polymerization (Figure 2c). These results demonstrate that complex **1** has a great potential for living polymerization.

As an application of the living polymerization, we successfully synthesized polyethylene-*b*-poly(ethylene-*co*-propylene) diblock copolymer and polyethylene-*b*-poly(ethylene-*co*-propylene)-*b*-polypropylene triblock copolymer by sequential addition of the monomers for the first time,[7] showing the usefulness of the titanium FI catalyst containing fluorine atoms in the ligands.

In summary, a new catalyst system for living ethylene polymerization at high temperatures has been introduced. The catalyst system promotes living ethylene polymerization at high temperatures and furnishes high molecular weight monodisperse polyethylene, displaying very high activity. With the catalyst system, a PE-*b*-(PE-*co*-PP) diblock copolymer and a PE-*b*-(PE-*co*-PP)-*b*-PP triblock copolymer have been prepared. The results described herein together with our previous reports[3] indicate that FI catalysts possess high potential for creating novel polymers. The results of polymerization using other olefins as well as mechanistic studies will be reported shortly.[8]

Experimental Section

Polyethylene synthesis: Ethylene polymerization was performed in a glass reactor (500 mL) equipped with a mechanical stirrer and a temperature probe. Toluene (250 mL) was introduced to the nitrogen-purged reactor and stirred (600 rpm). The toluene was thermostated to the prescribed polymerization temperature, and then the ethylene gas feed was started. After 10 min polymerization was initiated by the additions of 1.25 M MAO in toluene (1.0 mL, 1.25 mmol) and then 0.001 M **1** in toluene (0.5 mL, 0.5 μmol) to the reactor, unless otherwise noted. The polymerization was quenched after the prescribed time by the addition of isobutyl alcohol (10 mL). The resulting mixture was added to acidic methanol (1000 mL including 2 mL of conc. HCl). The polyethylene was collected by filtration, washed with methanol (2 × 200 mL), and then dried to constant weight (80 °C, vacuum oven).

The polydispersity (M_w/M_n) and number average molecular weight (M_n) of polyethylene were measured by gel permeation chromatography at 145 °C using polyethylene calibration.

1: ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.35$ (s, 18 H; *t*Bu), 7.02 (t, $^3J(H,H) = 7.6$ Hz, 2 H), 7.29 (dd, $^3J(H,H) = 7.6$, 1.6 Hz, 2 H), 7.64 (dd, $^3J(H,H) = 7.6$, 1.6 Hz, 2 H), 8.22 (s, 2 H; CH=N), 1.21 (t, $J =$ 7.0 Hz,($CH_3\mathit{CH_2}$)O), 3.48 (q, $J = 7.0$ Hz,($\mathit{CH_3}CH_2$)O); MS: *m*/*z* (%): 802 (100) [M^+]; elemental analysis calcd for $C_{34}H_{26}F_{10}Cl_2N_2O_2Ti + 1/3\,(C_2H_5)_2O$: 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.

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[4] Crystal data for complex **1** ($C_{34}H_{26}F_{10}Cl_2N_2O_2Ti + CH_2Cl_2$): $M_w =$ 888.31; crystal dimensions $0.40 \times 0.35 \times 0.07$ nm, monoclinic, $P2_1/n$, $a = 11.6786(2)$, $b = 25.6347(9)$, $c = 12.3467(1)$ Å, $\beta = 92.254(4)^\circ$, $V =$ 3693.5(1) Å^3, $Z = 4$, $\rho_{calcd} = 1.597$ g cm^{-3}, $2\theta_{max} = 59.9^\circ$, $F(000) = 1792$, $\mu(Mo_{K\alpha}) = 6.07$ cm^{-1}, Rigaku RAXIS-RAPID Imaging Plate, $Mo_{K\alpha}$ (λmax = 0.71069 Å), graphite monochromated, $T = -160$ °C, 32621 measured reflections, 9925 independent reflections, 9917 observed reflections($I > -3\sigma(I)$), The data were corrected for Lorentz and polarization effects, full-matrix least-squares refinement based on $|F^2|$, 487 parameters, hydrogen atom were included but not refined, $R1 =$ 0.048 (for 5207 data with $I > 2\sigma(I)$), $R(Rw) = 0.084$ (0.073), max./min. residual electron density 0.02/ – 0.02 e$^-$ Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159669. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] [Cp_2TiCl_2] produced polyethylenes having an M_w/M_n value of 3.31–3.45 under the conditions described in Figure 2, indicating that Cp_2TiCl_2 did not promote living polymerization under these conditions.

[6] Because the corresponding titanium complex without any fluorine atoms in the ligand produced polyethylene having an M_w/M_n value of about 2.0,[3b] it is obvious that the presence of the fluorine atoms is required for living polymerization. Density functional theory (DFT) calculations suggest that a fluorine atom adjacent to the imine nitrogen atom of an active species for polymerization interacts with a β-hydrogen atom of a polymer chain (β-H–F 2.28 Å), probably preventing β-hydrogen transfer. Thus, this interaction may be responsible for the realization of living polymerization.

[7] Polyethylene-*b*-poly(ethylene-*co*-propylene) diblock copolymer: PE M_n 115000, M_w/M_n 1.10, PE-*b*-(PE-*co*-PP), M_n 211000 M_w/M_n 1.16 polyethylene-*b*-poly(ethylene-*co*-propylene)-*b*-polypropylene triblock copolymer: PE M_n 115000, M_w/M_n 1.10, PE-*b*-(PE-*co*-PP) M_n 211000 M_w/M_n 1.16, PE-*b*-(PE-*co*-PP)-*b*-sPP ([rr] = 87%): M_n 235000, M_w/M_n 1.15.

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