Articles

Ethylene/Higher α-Olefin Copolymerization Behavior of Fluorinated Bis(phenoxy−imine)titanium Complexes with Methylalumoxane: Synthesis of New Polyethylene-Based Block Copolymers

Rieko Furuyama, Makoto Mitani, Jun-ichi Mohri, Ryoji Mori,
Hidetsugu Tanaka, and Terunori Fujita*

R&D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan

Received September 14, 2004; Revised Manuscript Received November 30, 2004

ABSTRACT: The catalytic behavior of fluorinated bis(phenoxy−imine)titanium complexes bearing a series of substituents *ortho* to the phenoxy oxygen was studied for ethylene and ethylene/higher α-olefin (i.e., 1-hexene, 1-octene, and 1-decene) (co)polymerizations. Independent of the magnitude of steric bulk of the *ortho*-substituent, all the complexes that were investigated produced polyethylenes (PEs) and ethylene/higher α-olefin copolymers with very narrow molecular weight distributions [e.g., PEs, $M_w/M_n = 1.05-1.16$, $M_n = 44000-412000$; ethylene/1-hexene copolymers, $M_w/M_n = 1.07-1.19$, $M_n = 49000-102000$, 1-hexene content 3.2−22.6 mol %], indicative of living polymerization. The incorporation ability for higher α-olefins is highly dependent on the nature of the *ortho*-substituent, and Ti complexes with a sterically less encumbered *ortho*-substituent incorporated a higher amount of higher α-olefins. A number of unique block copolymers consisting of highly linear PE and ethylene/1-hexene copolymer segments were prepared using one of the living catalysts with enhanced incorporating capability for higher α-olefins. These block copolymers exhibited lower peak melting temperatures (T_m) relative to the corresponding homo-PE. The molecular weight and 1-hexene content of the copolymer segment had a considerable effect on the T_m values of the resultant block copolymers. A polyethylene-*b*-poly(ethylene-*co*-1-hexene) ($M_w = 79900$, $M_w/M_n = 1.26$, 1-hexene content 4.3 mol %) possessed unique tensile properties with a good combination of extensibility and toughness compared to the corresponding blend and random (co)polymers.

Introduction

Since Doi's discovery of V-based catalysts[1] that promote living polymerization of propylene, a significant amount of research has been directed to the development of high-performance catalysts for living olefin polymerization. This is because of the ability of living olefin polymerization catalysts to synthesize precisely controlled polymers, ranging from monodisperse polymers and end-functionalized polymers to block copolymers with various compositions and molecular architectures. These living-polymerization-based polymers are anticipated to possess unique material properties that are unattainable in conventional polymers.

Remarkable progress in the rational design of transition-metal complexes for olefin polymerization and in polymerization techniques has led to the development of quite a few efficient and selective catalysts for living olefin polymerization.[2,3] These catalysts have allowed the production of a wide variety of living polymers, which include a large number of high molecular weight monodisperse polymers and block copolymers from ethylene and α-olefins.[4−8] However, only a limited number of catalysts have been developed so far, which form PE-based block copolymers.[4e−g,6q,8a−d,f,g] In particular, little has been reported about catalysts capable of producing block copolymers composed of highly linear PE and amorphous ethylene/higher α-olefin copolymer segments, which may display distinctive material properties due to the copresence of a crystalline PE segment and higher α-olefin-containing amorphous copolymer segment in the same molecule.

For our part, we have studied well-defined transition-metal complexes featuring nonsymmetric ligands with electronically flexible nature for viable olefin polymerization catalysts.[9−11] As a result, we found that fluorinated bis(phenoxy−imine)titanium complexes (fluorinated Ti-FI Catalysts) can mediate highly controlled, thermally robust living polymerization of both ethylene and propylene.[4f,g,5c,e,12] Coates et al. have independently reported a modified fluorinated Ti-FI Catalyst that can catalyze propylene polymerization in a living fashion.[5d,13] On the basis of DFT studies, we have proposed that an attractive interaction between a fluorine *ortho* to the imine nitrogen and a *β*-H on a growing polymer chain is responsible for the thermally robust living polymerization. The discovery of the fluorinated Ti-FI Catalysts has created new opportunities for the preparation of a wide array of living polymers. Recently, therefore, studies on the fluorinated Ti-FI Catalysts have been actively pursued in both academic and industrial research centers. Recent reviews summarize much of this work.[11e,f]

---

* To whom correspondence should be addressed. E-mail: Terunori.Fujita@mitsui-chem.co.jp.

10.1021/ma0481104 CCC: $30.25

As part of our studies on the development of higher performance Ti-FI Catalysts, we have investigated the polymerization behavior of a wide range of fluorinated Ti-FI Catalysts. These investigations furnished insight into the living nature and, in addition, resulted in the development of living Ti-FI Catalysts with high incorporation ability for higher α-olefins, which has enabled us to synthesize block copolymers from ethylene and higher α-olefins. In this paper, we describe the catalytic behavior of fluorinated Ti-FI Catalysts, which possess a series of substituents in the *ortho*-position on the phenoxy ring, for ethylene and ethylene/higher α-olefin (co)polymerizations. Additionally, we introduce the preparation of unique block copolymers comprised of highly linear PEs and ethylene/higher α-olefin copolymers, and the unique DSC behavior and tensile properties of the block copolymers produced. The results introduced herein further demonstrate the unique catalysis of fluorinated Ti-FI Catalysts and their ability to create value-added polymers.[11c,e]

Experimental Section

General Procedures and Materials. All operations involving air- and/or water-sensitive materials were conducted under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Anhydrous toluene was purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Complexes **1**−**5** were synthesized according to published procedures[5e] (for complex **2**, see the Supporting Information). The toluene that was used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3 under N_2. Polymerization grade ethylene gas was obtained from Sumitomo Seika Co., Ltd. 1-Hexene and 1-octene (Mitsubishi Chemical Corp.) and 1-decene (Wako Pure Chemical Industries, Ltd.) were dried over Al_2O_3 under N_2. Methylalumoxane (MAO) was purchased from Albemarle as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo, providing a solid white powder. All other chemicals were obtained commercially and used as supplied.

Ethylene Polymerization. Ethylene polymerization was carried out in a 500 mL glass reactor equipped with a propeller-like mechanical stirrer and a temperature probe. Toluene (250 mL) was introduced to the reactor and stirred (600 rpm) under a N_2 atmosphere. The toluene was kept at 25 °C, and then the ethylene gas feed (100 L/h) was started. After 10 min, polymerization was initiated by adding a toluene solution of MAO (1.25 M. 1 mL) and then an anhydrous toluene solution of a complex (**1**, 0.5 mM, 1 mL, 0.5 μmol; **2**−**5**, 5 mM, 1 mL, 5 μmol) into the reactor with stirring (600 rpm). After 1 min, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. The resulting mixture was poured into acidic methanol (1000 mL containing 2 mL of concentrated HCl). The polymer was collected by filtration, washed with methanol (200 mL × 2), and then dried in vacuo at 80 °C for 10 h.

Ethylene/Higher α-Olefin Copolymerization. Ethylene/higher α-olefin copolymerization was performed using the same type of equipment as the ethylene polymerization described above. Toluene (200 mL) and a higher α-olefin (1-hexene, 1-octene, or 1-decene, 50 mL) were introduced to the reactor and stirred (300 rpm) under a N_2 atmosphere. The solution was kept at 25 °C, and then a 1.25 M MAO solution in toluene (1 mL, 1.25 mmol) and a 2.5 mM complex solution in anhydrous toluene (1 mL, 2.5 μmol) were added to the solution. The ethylene gas feed (100 L/h) was started. After 5 min, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. The resulting mixture was poured into acidic methanol (1000 mL containing 2 mL of concentrated HCl). The polymer was collected by filtration, washed with methanol (200 mL × 2), and then dried in vacuo at 130 °C for 10 h.

Preparation of Polyethylene-*b*-poly(ethylene-*co*-1-hexene)s. Polyethylene-*b*-(ethylene-*co*-1-hexene)s were synthesized using the same type of equipment as the ethylene polymerization. Toluene (250 mL) was introduced to the reactor and stirred (300 rpm) under a N_2 atmosphere. The toluene was kept at 25 °C, and then the N_2 atmosphere was replaced with ethylene by an ethylene gas feed (100 L/h). After 10 min, the ethylene gas feed was stopped, and the toluene solution was kept under N_2 at 25 °C. To the resulting solution were added a 1.25 M MAO solution in toluene (2 mL, 2.5 mmol) and a 5 mM complex **4** solution in anhydrous toluene (4 mL, 20 μmol) to prepare a polyethylene segment. After 10 min, a prescribed amount of 1-hexene was added, and at the same time, the ethylene gas feed (50 L/h) was restarted to produce a poly(ethylene-*co*-1-hexene) segment. After a prescribed time, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. The resulting mixture was poured into acidic methanol (1000 mL containing 2 mL of concentrated HCl). The polymer was collected by filtration, washed with methanol (200 mL × 2), and then dried in vacuo at 130 °C for 10 h.

Preparation of a PE/Poly(ethylene-*co*-1-hexene) Blend. A mixture of PE ($M_n = 75300$, $M_w/M_n = 1.16$, 0.15 g), poly(ethylene-*co*-1-hexene) ($M_n = 77600$, $M_w/M_n = 1.10$, 1-hexene content 7.2 mol %, 0.15 g) and toluene (50 mL) in a 200 mL round-bottom flask was heated at a reflux temperature with stirring for 2 h. The resulting solution was poured into methanol (1 L, 25 °C). The precipitated polymer was collected by filtration, washed with methanol (20 mL × 2), and then dried in vacuo at 80 °C for 10 h.

Polymer Analyses. Molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined using a Waters GPC2000 gel permeation chromatograph equipped with four TSKgel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and two sets of TSKgelGMH$_6$−HTL) at 140 °C using polyethylene calibration. *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min.

^{1}H NMR spectra of the copolymers were recorded on a JEOL 270 (270 MHz) spectrometer from JEOL Co. Ltd. using 1,1,2,2-tetrachloroethane-d_2 as a solvent at 120 °C. Chemical shifts were referenced to the residual protio impurity of the deuterated solvent (δ 5.95 ppm). The amount of higher α-olefin incorporated was determined on the basis of the peak intensities of methyl (δ 0.93 ppm) and methylene and methine (δ 1.30 ppm) protons.

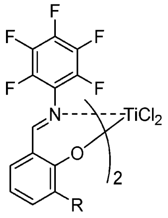
Peak melting temperatures (T_m) of the polymers were determined by DSC with a Shimadzu DSC-60 differential scanning calorimeter, measured upon reheating a polymer sample to 200 °C at a heating rate of 10 °C/min.

Tensile Properties of Polymers. Load-extension data of the polymers were obtained with an Intesco tensile instrument, model 210X, by uniaxially stretching at 23 °C, 50% relative humidity, and a constant strain of 50 mm/min, following ASTM D882-97. Samples were prepared by compression molding at 200 °C for 5 min under 11 MPa pressure between two aluminum plates with a 0.1 mm thickness spacer and then quenching at room temperature under the same pressure. Tensile specimens were cut to the dumbbell shape with a narrow midsection of 5 mm width and 30 mm length from the quenched sheets.

Results and Discussion

Ethylene Polymerization Behavior of Complexes 1−5 with MAO. In an attempt to gain information on the ethylene polymerization behavior of fluorinated bis(phenoxy−imine)titanium complexes, we decided to examine the effects of a substituent *ortho* to the phenoxy oxygen of the ligand. Since the *ortho*-substituent is situated in close proximity to the active site, the substituent may have an influence on the catalytic properties (e.g., catalytic activity, living nature, comonomer incorporation, comonomer distribution), which would throw further light on the catalysis of FI Catalysts.

Bis(phenoxy−imine)titanium complexes employed in this study [R = ^{t}Bu (**1**), cyclohexyl (**2**), ^{i}Pr (**3**), Me (**4**), H (**5**)] are shown in Figure 1, which were synthesized



Complex	R
1	^{t}Bu
2	cyclohexyl
3	^{i}Pr
4	Me
5	H

Figure 1. Titanium complexes **1**−**5** used in this study.

Table 1. Ethylene Polymerization with Complexes 1−5/MAO[a]

complex	yield (g)	TOF (min^{-1})	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	T_m[c] (°C)
1	0.283	20200	412	1.13	136
2	0.292	2080	49	1.05	134
3	0.323	2300	51	1.10	135
4	0.471	3360	75	1.16	136
5	0.211	1500	44	1.08	134

[a] Polymerization conditions: toluene, 250 mL; complex **1**, 0.5 μmol; complexes **2**−**5**, 5 μmol; MAO, 1.25 mmol; ethylene, 100 L/h; time, 1 min; temperature, 25 °C. [b] Determined by GPC using polyethylene calibration. [c] Determined by DSC.

either according to published procedures[4g] or in a similar manner via the reaction of $TiCl_4$ with the lithium salt of the corresponding phenoxy−imine ligand (see the Supporting Information). The ^{1}H NMR spectra of complexes **1**−**5** exhibit a single sharp peak attributed to the imine proton, which presumably indicates that these complexes exist as the C_2-symmetric isomer with a *trans*-O, *cis*-N, and *cis*-Cl disposition in solution though the nonfluorinated congeners normally exist as a mixture of this C_2-symmetric isomer and the C_1-symmetric isomer with a *cis*-O, *cis*-N, and *cis*-Cl arrangement.[10c,14]

We have already reported that complex **1** (R = ^{t}Bu) combined with MAO initiates living ethylene polymerization at 25 °C under atmospheric pressure.[4f,g] Results of ethylene polymerization with complexes **2**−**5** are presented in Table 1, which also includes the results for complex **1**. On analysis of the data listed in Table 1, several points emerge vis-à-vis the ethylene polymerization catalysis of the complexes. Complex **1**, which has the sterically most encumbered *ortho*-substituent (R = ^{t}Bu), is the most active of all the complexes examined in this research. There is, however, no clear correlation between the steric bulk of the substituent R and catalytic activity among complexes **2**−**5**. This may be due to the fact that the steric bulk can have two competing effects: (i) activity enhancement arising from an effective ion separation, induced by R, between the cationic active species and an anionic cocatalyst, (ii) activity decrease due to steric congestion, stemming from R, in close proximity to the active site.

Complexes **1**−**5** provided PEs possessing moderate to high molecular weights (M_n = 44000−412000). The PEs formed with these complexes exhibit T_m values in the range of 134−136 °C. ^{13}C NMR analyses indicate that the PEs have highly linear structures with practically no branching (branching of less than 1 per 1000 carbon atoms). Notably, all the complexes generated PEs with extremely narrow molecular weight distributions (M_w/M_n = 1.05−1.16), which is indicative of living polymerization. These facts suggest that, though the substituent R is located near the polymerization center, the steric hindrance provided by the substituent R exercises no significant influence on the living nature of the complexes under the conditions employed,[10c] implying that steric factors do not play a key role in the achievement of living ethylene polymerization with fluorinated Ti-FI Catalysts.[15] Assuming the presence of an electronically attractive interaction between the *o*-F and a *β*-H on a growing polymer chain (which effectively curtails chain transfer),[4g,11c] it is unsurprising that the steric obstacle in close proximity to the active site does not affect the living nature of the *o*-F−Ti complexes since electronic interactions play a pivotal role in the achievement of living polymerization. Indeed, DFT calculations show the proximity of a negatively charged *o*-F and a positively charged *β*-H for the catalytically active species derived from complexes **2**−**5** in addition to that from complex **1**. The calculated distances are 2.260−2.515 Å (see the Supporting Information), which indicates the presence of nonbonding attractive interaction, confirming the generality of such interaction between the two atoms.

Table 2. Ethylene and 1-Hexene Copolymerization with Complexes 1−5/MAO[a]

complex	yield (g)	TOF (min^{-1})	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	1-hexene content[c] (mol %)
1	0.167	448	54.5	1.19	3.2
2	0.172	396	49.0	1.14	12.0
3	0.327	745	82.5	1.12	12.6
4	0.374	788	102	1.12	17.7
5	0.211	414	54.2	1.07	22.6

[a] Polymerization conditions: toluene, 200 mL; complex, 2.5 μmol; MAO, 1.25 mmol; ethylene, 100 L/h; 1-hexene, 50 mL; time, 5 min; temperature, 25 °C. [b] Determined by GPC using polyethylene calibration. [c] Determined by ^{1}H NMR.

As a result of the above study, we have developed a series of living ethylene polymerization catalysts which possess a variety of steric environments near the polymerization center.

Ethylene/Higher α-Olefin Copolymerization Behavior of Complexes 1−5 with MAO. Although the steric bulk exerted by the substituent R *ortho* to the phenoxy oxygen has substantially no influence on the living nature of the complexes, the substituent should have an effect on the incorporation capability for α-olefins since the substituent is situated in close proximity to the active site.

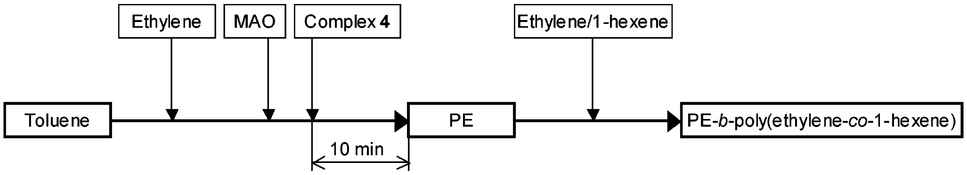
The ability of complexes **1**−**5** with MAO activation to mediate ethylene/1-hexene copolymerization was studied under atmospheric pressure. The relevant results are compiled in Table 2. All the complexes formed polymers, which range from semicrystalline to amorphous materials, with high productivity under the given conditions. These results indicate that the R substituent has a profound influence on the 1-hexene reactivity of the catalyst systems. The incorporation levels are in the range of 3.2−22.6 mol % (^{1}H NMR). Complex **5** (R = H) with MAO displayed the highest 1-hexene incorporation (22.6 mol %), followed by complexes **4** (R = Me, 17.7 mol %), **3** (R = ^{i}Pr, 12.6 mol %), **2** (R = cyclohexyl, 12.0 mol %), and **1** (R = ^{t}Bu, 3.2 mol %). A strong correlation exists between the magnitude of steric bulk provided by R and the incorporation ability for 1-hexene, and a decrease in the steric bulk led to an increase in the amount of 1-hexene incorporated. These results are probably associated with the fact that Ti complexes with smaller R substituents possess a sterically more open nature vis-à-vis polymerization. It is noted that complex **1** displays much lower activity in ethylene/1-hexene

Table 3. Ethylene and 1-Octene or 1-Decene Copolymerization with Complexes 1−5/MAO[a]

	ethylene/1-octene					ethylene/1-decene				
complex	yield (g)	TOF (min^{-1})	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	1-octene content[c] (mol %)	yield (g)	TOF (min^{-1})	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	1-decene content[c] (mol %)
1	0.234	612	62.3	1.22	3.0	0.256	684	76.1	1.20	1.7
2	0.214	476	60.3	1.13	9.4	0.295	632	65.4	1.13	8.3
3	0.408	910	102	1.13	9.3	0.390	848	108	1.14	7.8
4	0.442	915	110	1.15	12.6	0.574	1130	128	1.16	11.3
5	0.214	376	60.5	1.09	20.8	0.221	401	72.0	1.10	14.3

[a] Polymerization conditions: toluene, 200 mL; complex, 2.5 μmol; MAO, 1.25 mmol; ethylene, 100 L/h; 1-octene or 1-decene, 50 mL; time, 5 min; temperature, 25 °C. [b] Determined by GPC using polyethylene calibration. [c] Determined by ^{1}H NMR.

Scheme 1. Procedure for Polyethylene-*b*-poly(ethylene-*co*-1-hexene) Synthesis



copolymerization than in ethylene homopolymerization, which is probably due to the sterically more congested nature of the active site. GPC analyses show that the copolymers arising from complexes **1**−**5** with MAO have very narrow molecular weight distributions (M_w/M_n = 1.07−1.19), suggesting that the catalyst systems have the characteristics of a living ethylene/1-hexene copolymerization.

Ethylene/1-octene and ethylene/1-decene copolymerizations were also investigated using complexes **1**−**5** with MAO. The results of these studies are presented in Table 3. As expected, all the complexes produced copolymers with very narrow molecular weight distributions. Regarding comonomer reactivity, the same trend as for the ethylene/1-hexene copolymerization was observed with the catalyst systems. Namely, complex **5**/MAO displayed the highest incorporation capability for these higher α-olefins (1-octene, 20.8 mol %; 1-decene, 14.3 mol %), whereas **1**/MAO exhibited the lowest ability (1-octene, 3.0 mol %; 1-decene, 1.7 mol %). The results obtained with ethylene and ethylene/higher α-olefin (co)polymerizations using **1**−**5**/MAO suggest that, for fluorinated Ti-FI Catalysts, reduction in the bulkiness of the substituent R enhances reactivity toward higher α-olefins while maintaining the character of living polymerization. With these studies, we have obtained the fluorinated Ti-FI Catalysts that possess characteristics of living ethylene polymerization and, at the same time, high incorporation capability for higher α-olefins.

Synthesis of Block Copolymers from Ethylene and 1-Hexene. Having established the living nature of ethylene and ethylene/higher α-olefin (co)polymerizations with the fluorinated Ti-FI Catalysts, we decided to synthesize and determine the properties of a variety of block copolymers with different highly linear PE and ethylene/higher α-olefin segments. These block copolymers have potential uses in a broad range of applications that include compatibilizers, modifiers, elastomers, and composite materials.

A number of block copolymers from ethylene and higher α-olefins were synthesized with **4**/MAO using a sequential addition polymerization procedure (Scheme 1). Treatment of **4** (20 μmol)/MAO (2.5 mmol) with an ethylene-saturated toluene at 25 °C under a N_2 atmosphere for 10 min formed a living PE (M_n = 38300, M_w/M_n = 1.11, Table 4, B-0). Subsequently, 1-hexene (10 mL) was added to the reactor, and simultaneously, ethylene gas feed (50 L/h) was initiated. After 2.5 min of additional polymerization time, a well-defined polyethylene-*b*-poly(ethylene-*co*-1-hexene) was produced (M_n = 61500, M_w/M_n = 1.22, Table 4, B-1). Likewise, block copolymers having higher molecular weight copolymer segments were prepared by varying the polymerization time for the second copolymer segments (M_n = 79900, M_w/M_n = 1.26, Table 4, B-2; M_n = 121000, M_w/M_n = 1.31, Table 4, B-3).

Table 4. Preparation of Polyethylene-*b*-poly(ethylene-*co*-1-hexene)s (1)[a]

sample	time[b] (min)	yield (g)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]	T_m[d] (°C)	1-hexene content[e] (mol %)
B-0		0.804	38.3	1.11	135	
B-1	2.5	1.416	61.5	1.22	130	3.3 (8.8[f])
B-2	5	2.193	79.9	1.26	122	4.3 (8.3[f])
B-3	7.5	3.547	121	1.31	117	5.4 (7.9[f])

[a] Polymerization conditions: toluene, 250 mL; complex **4**, 20 μmol; MAO, 2.5 mmol; temperature, 25 °C. [b] Polymerization time of poly(ethylene-*co*-1-hexene) segments. [c] Determined by GPC using polyethylene calibration. [d] Determined by DSC. [e] 1-Hexene content of the block copolymer (determined by ^{1}H NMR). [f] 1-Hexene content of the poly(ethylene-*co*-1-hexene) segment (estimated from the 1-hexene content of the block copolymer and M_n).

The GPC traces of the living PE and polyethylene-*b*-poly(ethylene-*co*-1-hexene)s (Figure 2) indicate a shift toward the higher molecular weight region due to the subsequent copolymerization step without giving any peak in the low molecular weight region. These results demonstrate the formation of the targeted block copolymers. These are the first examples of polyethylene-*b*-poly(ethylene-*co*-1-hexene)s comprised of highly linear PE and poly(ethylene-*co*-1-hexene) segments, which were realized by the living nature of ethylene polymerization combined with the enhanced incorporating capability for higher α-olefins of the fluorinated Ti-FI Catalysts with the sterically less encumbered R substituent.

It is well-known that the peak melting temperature (T_m) correlates with the lamellar thickness and that the

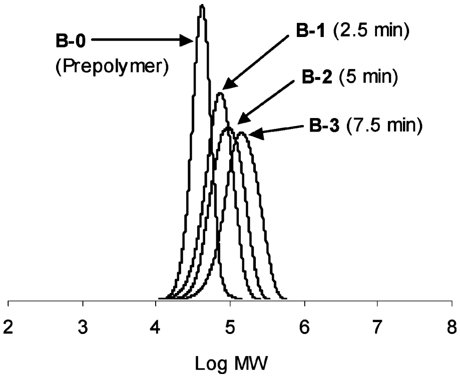


Figure 2. GPC curves for polyethylene-*b*-poly(ethylene-*co*-1-hexene) formation.

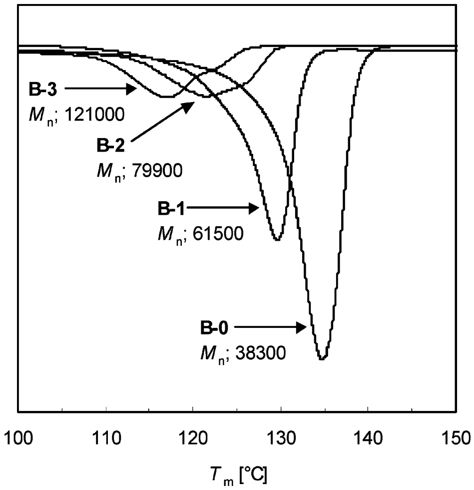


Figure 3. DSC curves for the polyethylene-*b*-poly(ethylene-*co*-1-hexene)s formed with **4**/MAO.

Table 5. Preparation of Polyethylene-*b*-poly(ethylene-*co*-1-hexene)s (2)[a]

sample	1-hexene vol (mL)	yield (g)	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	T_m[c] (°C)	1-hexene content[d] (mol %)
B-2	10	2.193	79.9	1.26	122	4.3 (8.3[e])
B-4	20	2.183	82.3	1.27	124	6.9 (12.9[e])
B-5	50	2.356	85.9	1.23	128	12.8 (23.1[e])
B-6	100	2.222	79.8	1.21	130	15.0 (28.9[e])

[a] Polymerization conditions: toluene, 250 mL; complex **4**, 20 μmol; MAO, 2.5 mmol; temperature, 25 °C. [b] Determined by GPC using polyethylene calibration. [c] Determined by DSC. [d] 1-Hexene content of the block copolymer (determined by ^{1}H NMR). [e] 1-Hexene content of the poly(ethylene-*co*-1-hexene) segment (estimated from the 1-hexene content of the block copolymer and M_n).

Table 6. Results of the Tensile Test of Compression-Molded Films, Block Copolymer (B-2), Blend Polymer, and Random Copolymer

	M_n[a] ($\times 10^3$)	E_m[b] (MPa)	σ_y[b] (MPa)	ϵ_y[b] (%)	σ_b[b] (MPa)	ϵ_b[b] (%)
B-2	79.9	119	7.59	13.9	26.0	488
blend[c]	75.3, 77.6	170	10.2	19.7	12.3	208
random	80.6	53.8	5.53	32.4	17.9	402

[a] Determined by GPC using polyethylene calibration. [b] E_m = elastic modulus, σ_y = stress at the yield point, ϵ_y = strain at the yield point, σ_b = stress at the break point, and ϵ_b = strain at the break point. [c] Blend ratio: PE/poly(ethylene-*co*-1-hexene) = 1/1 w/w.

enthalpy of fusion depends on the degree of crystallinity. DSC analyses showed that the block copolymers display T_m values in the range of 117−130 °C (Table 4), T_m values which are lower than that of the corresponding PE (T_m = 135 °C). The lower T_m values presumably originate from the incomplete phase separation of the crystalline PE block. An inspection of the data in Table 4 and Figure 3 suggests that the block copolymers possessing a higher molecular weight copolymer segment display lower T_m values and smaller enthalpies of fusion. These observations are consistent with the proposal that the crystallization process of the PE segment is disturbed by the presence of the chemically linked poly(ethylene-*co*-1-hexene) segment, providing thinner lamellar crystals and lower crystallinity. The thermal behavior described herein further confirms the generation of the desired block copolymers.

To obtain further information on ethylene- and 1-hexene-based block copolymers, we synthesized polyethylene-*b*-poly(ethylene-*co*-1-hexene)s possessing a variety of 1-hexene contents yet similar molecular weights of the copolymer segment. The relevant results (polymer yield, M_n, M_w/M_n, T_m, and 1-hexene content) are collected in Table 5. The data reveal the unique melting behavior of the block copolymers produced (for DSC charts, see the Supporting Information); that is, an increase in the 1-hexene content of the copolymer segment leads to an increase in T_m. These results indicate that a copolymer segment with a higher 1-hexene content (a softer copolymer segment) has less effect on the crystallization process of the PE segment, which is probably due to the reduced affinity between the two segments.

Since ethylene- and higher-α-olefin-based block copolymers with highly linear PE segments are novel materials, we preliminarily investigated the tensile properties of the polyethylene-*b*-poly(ethylene-*co*-1-hexene) made with **4**/MAO (B-2; M_n = 79900, M_w/M_n = 1.26, 1-hexene content 4.3 mol %). For comparison, the corresponding PE (M_n = 75300, M_w/M_n = 1.16)/poly(ethylene-*co*-1-hexene) (M_n = 77600, M_w/M_n = 1.10, 1-hexene content 7.2 mol %) blend polymer and poly(ethylene-*co*-1-hexene) random copolymer (M_n = 80600, M_w/M_n = 1.11, 1-hexene content 5.4 mol %) were also examined. The relevant results are summarized in Table 6.

The data confirmed the fragile nature of the blend polymer (ϵ_b = 208%), being due to the weak interfacial interactions between PE and poly(ethylene-*co*-1-hexene) components that are immiscible with each other. In addition, the data indicated that, as expected, the random copolymer is soft and, thus, easy to break (σ_b = 17.9 MPa), which stems from the absence of a highly crystalline PE component in the polymer.

Conversely, it was revealed that the block copolymer displays extensibility (ϵ_b = 488%) comparable or superior to those of the blend and random (co)polymers. Moreover, the block copolymer exhibits better toughness (E_m = 119 MPa) compared with the random copolymer. The tensile properties that were elucidated indicate that the block copolymer possesses both good extensibility and good toughness, probably because of the copresence of tough crystalline PE and soft poly(ethylene-*co*-1-hexene) segments in the same molecule. These results suggest that the block copolymers have high potential as materials for high impact strength films.

Conclusions

We have shown that, on activation with MAO, fluorinated bis(phenoxy−imine)titanium complexes having a H, a Me, an ^{i}Pr, a cyclohexyl, or a ^{t}Bu group *ortho* to the phenoxy oxygen can polymerize ethylene and ethylene/higher α-olefins in a living fashion at room temperature and produce highly linear PEs and ethylene/higher α-olefin copolymers with very narrow molecular weight distributions. While there is no clear relationship between the catalytic activity and the steric bulk of the *ortho*-substituent, a smaller substituent results in higher incorporation capability for higher α-olefins probably because of the sterically more open nature. It should be noted that the steric bulk of the *ortho*-substituent has practically no influence on the living nature of the catalyst systems under the conditions employed, implicating that steric factors do not play a key role in the achievement of living polymerization.

These complexes with MAO produce a wide array of unique block copolymers composed of highly linear PE and poly(ethylene-*co*-1-hexene) segments, which were previously unobtainable with conventional catalysts. The block copolymers exhibit $T_{\rm m}$ values (117−130 °C) lower than that of the corresponding PE ($T_{\rm m}$ = 135 °C), presumably due to the incomplete phase separation of the crystalline PE block. Additionally, it is revealed that PE-*b*-poly(ethylene-*co*-1-hexene)s having higher molecular weight copolymer segments display lower $T_{\rm m}$ values and that those with higher 1-hexene content of the copolymer segments exhibit higher $T_{\rm m}$ values. Finally, a polyethylene-*b*-poly(ethylene-*co*-1-hexene) is demonstrated to possess a good combination of extensibility and toughness.

The results described herein coupled with our previous reports[4f,g,5c,e,11c,e] show that the fluorinated Ti-FI Catalysts have made possible the syntheses of a wide range of polyolefinic materials with various compositions and unique architectures.

Acknowledgment. We thank Dr. M. Mullins for fruitful discussions and suggestions. We are also grateful to T. Tsutsui, J. Saito, Y. Suzuki, S. Ishii, H. Terao, T. Matsugi, and A. Valentine for their research and technical assistance. We also thank M. Onda for NMR analyses and T. Abiru for GPC analyses.

Supporting Information Available: Preparation of complex **2**, DFT calculation results of cationic active species, ^{1}H NMR spectra of the poly(ethylene-*co*-higher α-olefin)s, ^{13}C NMR spectrum of the poly(ethylene-*co*-1-hexene), and GPC profiles and DSC curves of the poly(ethylene-*co*-higher α-olefin)s (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814−819. (b) Doi, Y.; Ueki, S.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201−248.

(2) For a recent review see: Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257. For living olefin polymerization with phenoxy-based catalysts, see: Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1493−1517.

(3) Recent advances in the rational design of catalysts for living olefin polymerization have allowed the catalytic production of living-polymerization-based polymers; see; Mitani, M.; Mohri, J.; Furuyama, R.; Ishii, S.; Fujita, T. *Chem. Lett.* **2003**, *32*, 238−239.

(4) (a) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378−5380. (b) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990−10991. (c) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2001**, *34*, 1140−1142. (d) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633−2640. (e) Matsugi, T.; Matsui, S.; Kojoh, S.; Takagi, Y.; Inoue, Y.; Nakano, T.; Fujita, T.; Kashiwa, N. *Macromolecules* **2002**, *35*, 4880−4887. (f) 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. (g) 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. (h) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessenn, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522−523. (i) Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542−2544.

(5) (a) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665. (b) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184−3188. (c) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576−577. (d) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134−5135. (e) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293−4305. (f) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142−3145. (g) Hagimoto, H.; Shiono, T.; Ikeda, T. *Macromol. Chem. Phys.* **2004**, *205*, 363−369.

(6) (a) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009. (b) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831. (c) Scollard, J. D.; McConville, D. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal. A* **1998**, *128*, 201−214. (d) Jeon, Y.-M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 3161−3163. (e) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649−3670. (f) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959. (g) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706−10707. (h) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Chem. Commun.* **2001**, 2120−2121. (i) Schrock, R. R.; Adamchuk, J. Ruhland, K. Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079−5091. (j) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197−6198. (k) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754−10755. (l) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746−10747. (m) Nomura, K.; Fudo, A. *J. Mol. Catal. A* **2004**, *209*, 9−17. (n) Jansen, J. C.; Mendichi, R.; Sacchi, M. C.; Tritto, I. *Macromol. Chem. Phys.* **2003**, *204*, 522−530. (o) Li, X. F.; Dai, K.; Ye, W. P.; Pan, L.; Li, Y. S. *Organometallics* **2004**, *23*, 1223−1230. (p) Yoshida, Y.; Saito, J.; Mitani, M.; Takagi, Y.; Matsui, S.; Ishii, S.; Nakano, T.; Kashiwa, N.; Fujita, T. *Chem. Commun.* **2002**, 1298−1299. (q) Yoshida, Y.; Mohri, J.; Ishii, S.; Mitani, M.; Saito, J.; Matsui, S.; Makio, H.; Nakano, T.; Tanaka, H.; Onda, M.; Yamamoto, Y.; Mizuno, A.; Fujita, T. *J. Am. Chem. Soc.* **2004**, *126*, 12023−12032.

(7) Liu, B.; Matsuoka, H.; Terano, M. *Macromol. Rapid Commun.* **2001**, *22*, 1−24.

(8) (a) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115−5116. (b) Desurmont, G.; Tokimitsu, T.; Yasuda, H. *Macromolecules* **2000**, *33*, 7679−7681. (c) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811−1813. (d) Turner, H. W.; Hlatky, G. G. (Exxon). PCT International Application 9112285, 1991; *Chem. Abstr.* **1992**, *116*, 61330t. (e) Kojoh, S.; Matsugi, T.; Saito, J.; Mitani, M.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 822−823. (f) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2003**, *36*, 3085−3100. (g) Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Togrou, M. *Macromolecules* **2003**, *36*, 3806−3808.

(9) (a) Inoue, Y.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 1060−1061. (b) Suzuki, Y.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2002**, 358−359. (c) Suzuki, Y.; Inoue, Y.; Tanaka, H.; Fujita, T. *Macromol. Rapid Commun.* **2004**, *25*, 493−497. (d) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Organometallics* **2001**, *20*, 4793−4799. (e) Yoshida, Y.; Nakano, T.; Tanaka, H.; Fujita, T. *Isr. J. Chem.* **2002**, *42*, 353−359.

(10) (a) Saito, J.; Mitani, M.; Matsui, S.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2000**, *21*, 1333−1336. (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) Furuyama, R.; Saito, J.; Ishii, S.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Matsukawa, N.; Tanaka, H.; Fujita,

T. *J. Mol. Catal. A* **2003**, *200*, 31−42. (d) Tohi, Y.; Makio, H.; Matsui, S.; Onda, M.; Fujita, T. *Macromolecules* **2003**, *36*, 523−525. (e) Makio, H.; Tohi, Y.; Saito, J.; Onda, M.; Fujita, T. *Macromol. Rapid Commun.* **2003**, *24*, 894−899. (f) Prasad, A. V.; Makio, H.; Saito, J.; Onda, M.; Fujita, T. *Chem. Lett.* **2004**, *33*, 250−251. (g) Nakayama, Y.; Bando, H.; Sonobe, Y.; Kaneko, H.; Kashiwa, N.; Fujita, T. *J. Catal.* **2003**, *215*, 171−175. (h) Tohi, Y.; Nakano, T.; Makio, H.; Matsui, S.; Fujita, T.; Yamaguchi, T. *Macromol. Chem. Phys.* **2004**, *205*, 1179−1186.

(11) (a) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477−493. (b) Matsukawa, N.; Ishii, S.; Furuyama, R.; Saito, J.; Mitani, M.; Makio, H.; Tanaka, H.; Fujita, T. *e-Polymers* [Online] **2003**, No. 021 (http://www.e-Polymers.org). (c) Mitani, M.; Nakano, T.; Fujita, T. *Chem.−Eur. J.* **2003**, *9*, 2396−2403. (d) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 617−625. (e) Mitani, M.; Saito, J.; Ishii, S.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *Chem. Rec.* **2004**, *4*, 37−158. (f) Makio, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 52−66.

(12) 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 (filing date Jan 26, 2000).

(13) Coates, G. W.; Tian, J.; Hustad, P. D. US Pat. 6562930, 2003 (filing date Sept 18, 2001).

(14) The possibility cannot be ruled out that the NMR behavior stems from a rapidly equilibrating mixture of isomers, on the NMR time scale, though DFT calculations suggest the complexes virtually exist as a single C_2-symmetric isomer.

(15) It has been demonstrated that, although the first discovery of the living behavior was made with a pentafluorinated version of the catalysts (see ref 4f), only a single *o*-F is a requirement for the living polymerization of ethylene, and the corresponding non-F and *o*-methylated versions do not promote living ethylene polymerization under identical conditions (see refs 4g and 10c). These results indicate that steric factors do not play a key role in the achievement of living ethylene polymerization.

MA0481104