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New Titanium Complexes with Two *β*-Enaminoketonato Chelate Ligands: Syntheses, Structures, and Olefin Polymerization Activities

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New titanium complexes with two nonsymmetric bidentate *β*-enaminoketonato (N,O) ligands (**4a**−**e**), $[(Ph)NC(R_2)C(H)C(R_1)O]_2TiCl_2$, have been synthesized. X-ray crystal structure reveals that complex **4a** has a C_2-symmetric conformation with a distorted octahedral geometry around the titanium center. With modified methylaluminoxane (MMAO) as a cocatalyst, complexes **4a**−**e** are active catalysts for ethylene polymerization at room temperature, producing high molecular weight polyethylenes bearing linear structures. The **4a**,**b**/MMAO catalyst systems exhibit the characteristics of a quasi-living polymerization of ethylene, producing polyethylenes with narrow molecular weight distributions. Moreover, the **4a**−**d**/MMAO catalyst systems are also capable of promoting the quasi-living copolymerization of ethylene with norbornene at room temperature, yielding high molecular weight alternating copolymers with narrow molecular weight distributions. The quasi-living nature of the catalysts allows the synthesis of new A−B polyethylene-*block*-poly(ethylene-*co*-norbornene) diblock copolymer.

Introduction

Living polymerization has attracted much attention for synthesizing monodisperse polymers, terminally functionalized polymers, and block copolymers.[1] Recently, several papers have reported on the living olefin polymerization promoted by well-defined or single-site transition metal catalysts.[2−6] However, there are few examples for the living polymerization of olefins at room temperature.[7−9] More recently, Fujita, Coates, and Pellecchia developed a class of single-site titanium catalysts that exhibited unprecedented scope for the living (co)polymerization of olefins at room temperature.[10−12] Most interest was drawn on the titanium catalysts based on chelating bis(phenoxyimine),[10] bis(indolideimine),[11] and bis(pyrrolideimine) ligands,[12] while *β*-enaminoketonato-based titanium catalysts have attracted more limited attention. Moreover, as reported by Fujita, the nonfluorinated bis(phenoxyimine) tita-

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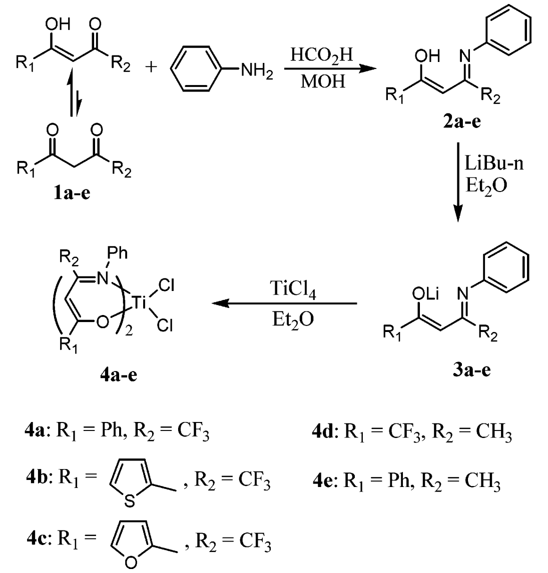
Scheme 1. Synthesis of Titanium Complexes 4a−e



nium catalysts do not promote living ethylene polymerization at room temperature; only the corresponding titanium complexes having fluorine atom(s) adjacent to the imine nitrogen can promote living ethylene polymerization under similar conditions.[10f]

The fact that variation of the ligand structure may lead to profound changes in the catalytic activity and the property of polymer prompts us to introduce the nonsymmetric bidentate β-enaminoketonato ligands to group 4 transition metal chemistry. β-Enaminoketonato ligands are among the most ubiquitous chelating systems in coordination chemistry because of their ease of preparation and simple modification of both steric and/or electronic effects. The new nonsymmetric bidentate β-enaminoketonato ligands were chosen because they contained the desired anionic [N,O] chelate, a nonfluorinated *N*-aryl group, and the different substituents at the R_1 and R_2 positions. Using these ligands, we report here the synthesis and characterization of the new titanium complexes and their application as efficient catalysts for the quasi-living ethylene polymerization and the quasi-living copolymerization of ethylene with norbornene.

Results and Discussion

A. Synthesis and Structure of Titanium Complexes Bearing Two β-Enaminoketonato Chelate Ligands. A general synthetic route for new titanium complexes used in this study is shown in Scheme 1. β-Enaminoketonates **2a**−**e** were obtained in good yields (**2a**, 66.7%; **2b**, 73.5%; **2c**, 67.2%; **2d**, 41.0%; **2e**, 80.0%) by the condensation of corresponding β-diketonates **1a**−**e** with aniline in methanol containing a little formic acid as the catalyst. The reason only β-enaminoketonates **2a**−**e** can be formed is that the β-diketonates **1a**−**c** exhibit keto−enol tautomerism and R_1 representing an aryl or a trifluoromethyl group with great electron-drawing effect increases the enol percentage, and/or there is a steric effect between the bulky R_1 and *N*-aryl group in the β-enaminoketonates. Desired titanium complexes **4a**−**e** were prepared under moderate conditions in good yields (**4a**, 81.1%; **4b**, 78.2%; **4c**, 76.5%; **4d**, 85.2%; **4e**, 90.4%) by the reaction of $TiCl_4$ with 2 equiv of the lithium salts of β-enaminoketonates **3a**−**e** in dried diethyl ether.

Table 1. Crystal Data and Structure Refinements for Complex 4a

empirical formula	$C_{32}H_{22}Cl_2F_6N_2O_2Ti$
fw	699.32
cryst syst	monoclinic
space group	$C2/c$
a (Å)	21.950(4)
b (Å)	8.3331(5)
c (Å)	17.033(3)
V (Å^3)	3114.4(8)
Z	4
density(calc) (Mg/cm^3)	1.492
abs coeff (mm^{-1})	0.515
F(000)	1416
cryst size (mm)	0.48 × 0.36 × 0.32
θ range (deg)	1.86 to 26.02
indep reflns	3059 ($R_{\mathrm{int}} = 0.0224$)
absorp corr	psi-scan
max. and min. transmn	0.4785 and 0.4296
no. of data/restraints/params	3059/0/204
goodness-of-fit on F^2	0.950
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0404$, $wR_2 = 0.0643$
largest diff peak and hole (e/Å^{-3})	0.264 and −0.287

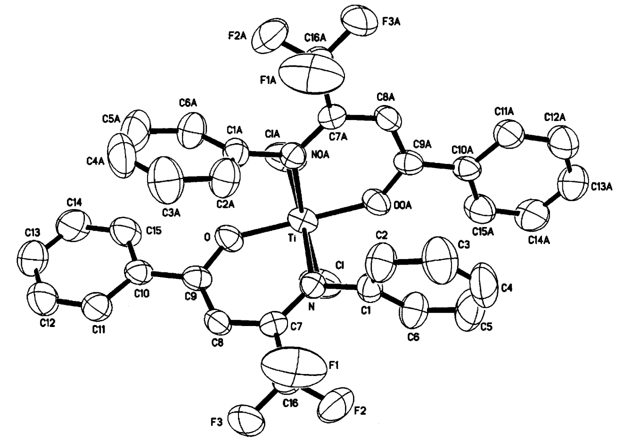


Figure 1. ORTER drawing of the molecular structure of complex **4a** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−Cl(A), 2.2695(11); Ti−O(A), 1.8739(18); Ti−N(A), 2.209(2); N−C(7), 1.313(3); O−C(9), 1.305(3); O−Ti−OA, 166.25(13); N−Ti−NA, 88.74(12); Cl−Ti−Cl(A), 95.996(6); O(A)−Ti−N(A), 81.52(8); O(A)−Ti−Cl(A), 95.68(6); N(A)−Ti−Cl(A), 87.83(6); O−Ti−NA, 88.65(9); N−Ti−Cl, 174.03(7); O−Ti−Cl(A), 93.51(6); C(9)−O−Ti, 140.8(2); C(7)−N−Ti, 124.1(2).

A crystal of complex **4a** suitable for X-ray structure determination was grown from a diethyl ether−hexane (1:6) solution. The crystallographic data, collection parameters, and refinement parameters are summarized in Table 1. In the solid state, the molecular structure of complex **4a** belongs to the C_2-symmetric system with a distorted octahedral geometry around the titanium center (Figure 1), like Fujita's catalyst with two nonfluorinated phenoxy-imine chelate ligands.[13] The two oxygen atoms are situated in the *trans* position (O−Ti−O angle, 166.25(13)°), while the two nitrogen atoms are in the *cis* position to each other and so are the two chlorine atoms (N−Ti−N angle, 88.74(12)°; Cl−Ti−Cl angle, 95.99(6)°) at the central titanium metal.

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Table 2. Polymerization of Ethylene by the 4a−e/MMAO Systems[a]

entry	complex (μmol)	Al/Ti[b]	time (mim)	temp (°C)	polymer (g)	activity[c]	T_m[d] (°C)	$\bar{M}_n$[e] ($\times 10^4$)	$\bar{M}_w/\bar{M}_n$[e]
1	**4a** (1)	2000	5	25	0.11	1.32	134	6.1	1.27
2	**4b** (3)	2000	5	25	0.17	0.68	135	5.0	1.34
3	**4c** (3)	2000	5	25	0.08	0.32	134	0.8	9.76
4	**4d** (3)	2000	5	25	0.27	1.08	136	6.1	2.56
5	**4e** (3)	2000	5	25	0.05	0.12	134	n.d.	n.d.
6	**4a** (1)	1500	5	25	0.09	1.08	137	5.9	1.28
7	**4a** (1)	1250	5	25	0.08	0.96	139	9.1	1.28
8	**4a** (1)	1000	5	25	0.02	0.24	140	n.d.	n.d.
9	**4a** (1)	2000	5	50	0.15	0.60	134	3.1	2.30
10	**4a** (1)	2000	5	70	0.08	0.30	131	1.1	3.64
11	**4a**[f] (5)	2000	35	25	0.10		139	9.6	1.30
12	**4a**[g] (5)	2000	67	25	0.30		139	12.9	1.37
13	FI catalyst (0.5)[10f]	1250	1	25	0.28	33.60		41.2	1.13

[a] Reaction conditions: 1 atm ethylene pressure, toluene 100 mL. [b] Molar ratio. [c] Activity, kg of PE/mmol of cat·h. [d] Measured by DSC. [e] Determined by GPC using polystyrene standard. [f] Under nitrogen atmosphere, the polymerization was conducted for 35 min in ethylene-saturated toluene. [g] Under nitrogen atmosphere, the polymerization in ethylene-saturated toluene was conducted for 65 min, then ethylene was again added, and the polymerization was carried out for another 2 min.

The Ti−O (1.8739(18) Å), Ti−N (2.209(2) Å), and Ti−Cl (2.2695(11) Å) bond distances are the same for the two ligands in complex **4a** and similar to that of Fujita's catalyst with two nonfluorinated phenoxy-imine chelate ligands, i.e., Ti−O bond distance (1.852(4) and 1.851(4) Å), Ti−N bond distance (2.236(4) and 2.213(4) Å), and Ti−Cl bond distance (2.305(2) and 2.296(2) Å).[13]

B. Ethylene Polymerization Behavior of Complexes 4a−e/MMAO Systems. With modified methylaluminoxane (MMAO) as a cocatalyst, new titanium complexes **4a**−**e** have been investigated as effective catalysts for ethylene polymerization at room temperature under atmospheric pressure. The results are summarized in Table 2. The data of entries 1−5 demonstrate that the change of substituents R_1 or/and R_2 affects significantly the catalytic activity. With an electron-withdrawing trifluoromethyl group at the R_2 position, complex **4a** (R_1 = Ph) displayed a very high catalytic activity of 1.32 kg of polyethylene (PE)/mmol of cat·h ($\bar{M}_n = 6.1 \times 10^4$, entry 1). Complexes **4b** (R_1 = 2-thenoyl) and **4c** (R_1 = 2-furyl), which have an electron-donating group containing a sulfur or oxygen atom at the R_1 position, exhibited moderate catalytic activities of 0.68 ($\bar{M}_n = 5.0 \times 10^4$, entry 2) and 0.32 kg of PE/mmol of cat·h ($\bar{M}_n = 0.8 \times 10^4$, entry 3), respectively. In contrast, with the replacement of the phenyl group at the R_1 position with a trifluoromethyl group, complex **4d** ($R_2 = CH_3$) also displayed a high catalytic activity of 1.08 kg of PE/mmol of cat·h ($\bar{M}_n = 6.1 \times 10^4$, entry 4). However, the catalytic activity of complex **4e** (R_1 = Ph, $R_2 = CH_3$) decreased to 0.12 kg of PE/mmol of cat·h under the same conditions (entry 5). The comparisons of **4a** with **4e**, **4a** with **4b** and **4c**, and **4d** with **4e** indicate that the introduction of an electron-withdrawing group at the R_1 or/and R_2 position can considerably increase the catalytic activity.

The result of ethylene polymerization with a typical titanium complex possessing a pentafluorine-containing phenoxy-imine chelate ligand (FI catalyst), as a comparison, is also listed in Table 2 (entry 13).[10f] As reported, catalytic activities and molecular weight distributions of the polyethylenes obtained are greatly affected by the number and the location of the fluorine atom(s) in the ligand.[10f] At 25 °C, the activity of FI catalyst was found to be higher than that of the complex **4a**, probably ascribed to the electron-withdrawing effect of fluorine in *N*-aryl, resulting in a more electrophilic titanium center. Moreover, the polyethylene obtained with FI catalyst possesses a narrower molecular weight distribution and higher molecular weight than those of polyethylenes obtained by complex **4a**, which is due to the fluorine adjacent to the imine nitrogen suppressing the β-hydrogen transfer. For FI catalysts with no fluorine adjacent to the imine nitrogen, the molecular weight distributions of the polyethylenes obtained will be broader, and the values increase to 2.0.[10f] Considering that the presence of fluorine atom(s) adjacent to the imine nitrogen is a requirement for the room-temperature or high-temperature living polymerization for the FI catalyst systems, we also tried to synthesize titanium complexes bearing β-enaminoketonato ligands with fluorine in *N*-aryl. Unfortunately, we did not succeed.

The polyethylenes produced by **4a**−**e**/MMAO systems exhibit melting temperatures (T_m) in the range 134−136 °C. The ^{13}C NMR analyses indicate that the polyethylenes have linear structures with virtually no branching. The molecular weight distributions of the polyethylenes obtained by complexes **4a** and **4b** are narrow ($\bar{M}_w/\bar{M}_n$ = 1.27 and 1.34, respectively), which suggests that the polymerization reactions of ethylene promoted by **4a**,**4b**/MMAO catalyst systems have the characteristics of quasi-living polymerization.

To confirm the quasi-living nature of the catalyst systems, postpolymerizations were conducted with **4a**/MMAO system according to the procedure reported by Fujita.[10f] The results are summarized in Table 2 (entries 11, 12). Treatment of **4a**/MMAO with ethylene-saturated toluene at room temperature under nitrogen atmosphere caused the polymerizations to continue for 35 and 65 min (the ethylene was substantially consumed within 5 min). After a prescribed time, the previous polymerization system was stopped and the next polymerization system further introduced the ethylene gas feed for 2 min to result in the formation of polyethylene having a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.37). The GPC curves of entries 11 and 12 are illustrated in Figure 2. The GPC curve of entry 12 shifted to higher molecular weight range, and no peak or shoulders were observed in the range of that of entry 11, although the $\bar{M}_w/\bar{M}_n$ value somewhat increased. These results indicate that the catalyst lifetime is longer than 60 min, even in the absence of ethylene. Therefore, the catalyst systems indeed conducted quasi-living polymerization of ethylene.

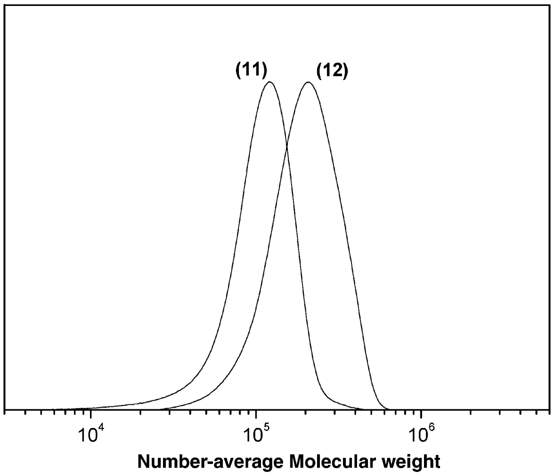

Figure 2. GPC profiles of the polyethylenes obtained by the postpolymerization with the **4a**/MMAO system.

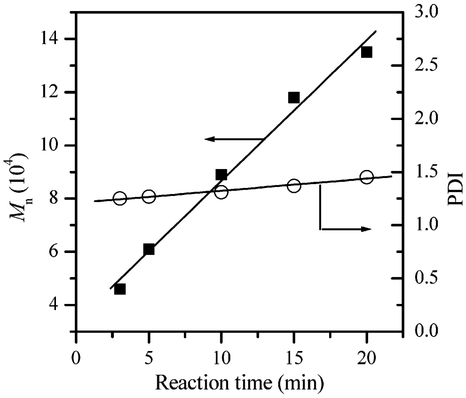

Figure 3. Dependences of number-average molecular weights (■) and molecular weight distributions (○) on polymerization time using complex **4a** in the ethylene polymerization at 25 °C at atmospheric pressure (Al/Ti = 2000/1).

To further confirm the quasi-living nature of the catalyst systems, the polymerizations of ethylene promoted by the **4a**/MMAO system were carried out with variations of the reaction parameters such as Al/Ti ratio, polymerization reaction time, and temperature. The results are also collected in Table 2 (entries 1, 6−10). The data of entries 1 and 6−8 indicate that the increase of the Al/Ni molar ratio improved the catalytic activity of complex **4a** at the expense of the molecular weights of the polymers. However, the molecular weight distributions stayed about 1.28, suggesting that the polymerization of ethylene catalyzed by the **4a**/MMAO system was quasi-living.

As shown in Figure 3, with an increase in polymerization time, the linear relationships between $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ and polymerization time as well as the narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.25−1.45) were obtained. The reason a long reaction time may cause undesirable broadening of the molecular weight distribution is that the catalyst systems are highly active for ethylene polymerization and excess polymer precipitation results in the nonhomogenity of the polymerization system, which had been discussed by Fujita.[10f] Some molecules of the catalysts could be enwrapped by the precipitated polyethylenes. Thus, with the increase of polymerization time, the diffusion of ethylene will control the rate of ethylene polymerization to some extent, which results in the gradual broadening of the molecular weigh distribution of polyethylene and the gradual decrease of catalyst activity. However, the GPC curves of the polyethylenes produced shifted to the higher molecular weight region with an increase of polymerization time, while the monomodal shape was retained, which indicates that the polymerization proceeded in a quasi-living fashion even at a longer polymerization time.

The temperature has significant effects on the properties of polyethylenes obtained (entries 1, 9, and 10). At 50 °C, the polyethylene has a low molecular weight ($\bar{M}_n = 3.1 \times 10^4$) and a broad molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 2.30). Moreover, at 70 °C, the polyethylene obtained has the lowest T_m's with the broadest molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 3.64). These results indicate that an increase of reaction temperature causes chain termination or transfer and/or catalyst deactivation, resulting in the loss of the quasi-living character of the polymerization reaction of ethylene promoted by the **4a**/MMAO system.

C. Ethylene/Norbornene Copolymerizations Catalyzed by 4a−d/MMAO Systems. At room temperature, **4a**−**d**/MMAO systems also show very efficient catalytic activity for the quasi-living copolymerization of ethylene with norbornene. The results are summarized in Table 3. It is very interesting that the copolymerization activity is similar to that of ethylene homopolymerization of these titanium catalysts. Of the four catalyst systems, complex **4d** exhibited the highest catalytic activity of 3.20 kg of polymer/mmol of cat·h (entry 4), followed by complex **4a** (1.72 kg of polymer/mmol of cat·h) (entry 1). Complexes **4b** and **4c** displayed a lower catalytic activity (0.58 and 0.44 kg of polymer/mmol of cat·h, respectively, entries 2 and 3) by almost an order of magnitude less than those of complexes **4a** and **4d**. The low catalytic activities may be due to the presence of a group containing an S or an O strong electron-donating atom at the R_1 position.

The GPC analyses reveal that the copolymers obtained possess high molecular weights ($\bar{M}_n = (1.5-5.7) \times 10^5$) and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.17−1.35), indicating that **4a**−**c**/MMAO systems have the characteristics to catalyze the quasi-living copolymerization of ethylene with norbornene under moderate conditions. The E/N copolymers obtained have T_g values between 121 and 135 °C, determined by means of DSC techniques. The microstructures of copolymers have been investigated using NMR techniques. The ^{13}C NMR spectra all show five major signals, which appear very close to the one for a copolymer synthesized by the $[2\text{-}(PhNCH)C_4H_3N]_2TiCl_2$/MAO catalytic system reported by Fujita,[12] as expected for an alternating copolymer. In Figure 4, the copolymer catalyzed by complex **4d** has high norbornene incorporation, about 48.7 mol %, and should be almost completely alternating in the absence of NN sequences. Moreover, complexes **4a** and **4b** incorporate norbornene into the copolymers with similar efficiencies (44.3 and 46.4 mol %, respectively), while complex **4c** incorporates norbornene into the copolymers at about 35 mol % at similar feed ratio.[14] The integration of carbons 1 and 2 due to the NENEN sequences reveals that the copolymers contain similar amounts of *meso* and *racemic*

Table 3. Copolymerization of Ethylene with Norbornene Promoted by the 4a−d/MMAO Catalytic Systems[a]

entry	complex	NB (g)	V (mL)	T (°C)	product (g)	activity[b]	NB content[c] (mol %)	T_g[d] (°C)	$\bar{M}_n$[e] ($\times 10^5$)	$\bar{M}_w/\bar{M}_n$[e]
1	**4a**	5.00	80	25	0.86	1.72	44.3	121	3.4	1.17
2	**4b**	5.00	80	25	0.29	0.58	46.4	125	1.9	1.19
3	**4c**	5.00	80	25	0.22	0.44	35.3	123	1.5	1.35
4	**4d**	5.00	80	25	1.60	3.20	48.7	135	5.7	1.54
5	**4d**	1.25	80	25	0.63	1.26	36.0	115	5.3	1.46
6	**4d**	2.50	80	25	0.64	1.28	41.0	141	3.0	1.51
7	**4d**	5.00	80	0	0.51	1.02	42.8	121	3.5	1.19
8	**4d**	5.00	80	50	0.67	1.34	49.0	142	3.3	1.91
9	**4d**	5.00	40	25	1.41	2.82	53.3	143	5.4	1.45
10	**4d**	5.00	20	25	1.18	2.36	55.4	144	4.8	1.38
11[f]	**4a**	5.00	100	2	0.26		11.1	137[g]	1.4	1.38

[a] Reaction conditions: 1 atm ethylene pressure; 3 μmol of cat.; Al/Ti = 2000/1; polymerization for 10 min. [b] Activity, kg of polymer/mmol of cat·h. [c] Norbornene contents were determined by ^{13}C NMR. [d] Measured by DSC. [e] Determined by GPC. [f] The polymerization was conducted in ethylene-saturated toluene for 5 min, and then norbornene and ethylene were introduced simultaneously, and the polymerization was carried out for 5 min to prepare a A−B diblock copolymer. [g] T_m of block copolymer determined by DSC.

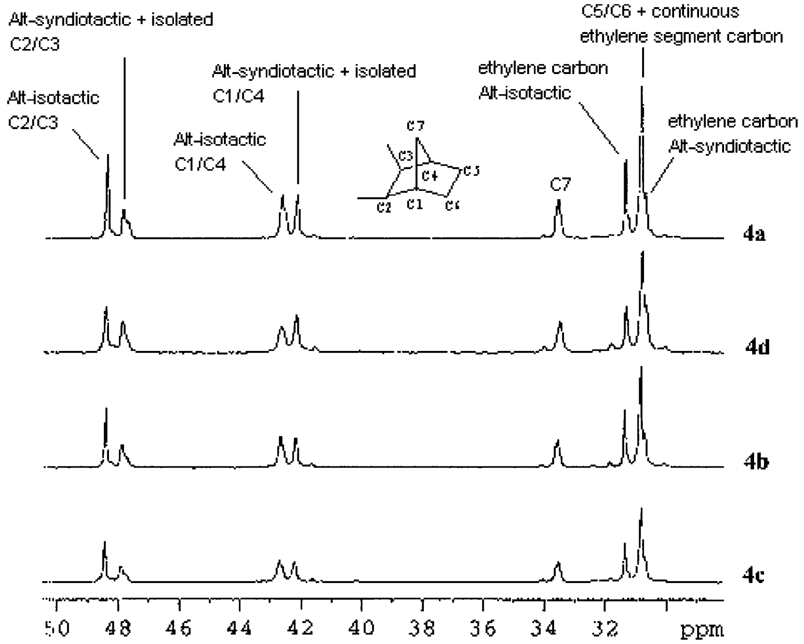

Figure 4. ^{13}C NMR of the copolymers obtained by the **4a−d**/MMAO catalytic systems.

sequences (isotactic/syndiotactic: entry 1, 57.4/42.6; entry 2, 56.2/43.8; entry 3, 59.9/40.1; entry 4, 47.7/52.3).[15]

The copolymerizations of ethylene with norbornene were also carried out with variation of the reaction parameters in order to investigate the quasi-living nature of the copolymerization reaction promoted by the **4d**/MMAO system (Table 3, entries 5−10). Catalytic activities and the molecular weights of the copolymers were considerably affected by the quantities of norbornene charged (entries 4−6). Furthermore, with the increase of the quantity of norbornene charged, the norbornene contents of the copolymers rose from 36.0 to 48.7%. It is noteworthy that a detailed inspection of the spectra of entry 5 reveals the signals of isolated norbornene units (from EENEE sequences, about 35.4%, see Supporting Information). However, the molecular weight distributions of the copolymers stayed about 1.50 all the way. Table 3 also collects the results of the copolymerization of ethylene with norbornene as a function of temperature (entries 4, 7, and 8). As a result, the activity of complex **4d** and the molecular weight of the copolymers reached a maximum (3.20 kg of polymer/mmol of cat·h and $\bar{M}_n = 5.7 \times 10^5$) at 25 °C. The norbornene content gradually increased from 42.8% to 49.0% with the increase of polymerization temperature (from 0 to 50 °C). Moreover, the molecular weight distributions of the copolymers changed dramatically. At 0 °C, the molecular weight distribution was very narrow (1.19). However, with the increase of temperature, the molecular weight distribution also increased from 1.19 to 1.91, which suggests that low temperature favors the quasi-living copolymerization of ethylene with norbornene. The monomer concentration also has a significant influence on the copolymerization reaction behavior (entries 4, 9, and 10). When the total volume was reduced from 80 mL to 20 mL, the catalytic activities decreased from 3.20 to 2.36 kg of polymer/mmol of cat·h. It is very interesting that the norbornene contents in the copolymers increased slightly and ex-

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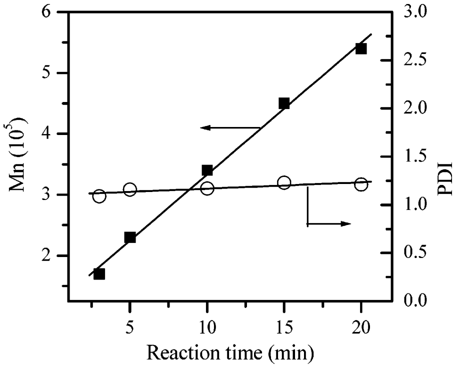

Figure 5. Dependences of number-average molecular weights (■) and molecular weight distributions (○) on polymerization time with complex **4a** as the catalyst in the copolymerization of ethylene and norbornene at 25 °C at atmospheric pressure (Al/Ti = 2000/1).

ceeded 50% by decreasing the volume of toluene. Compared with the spectra as mentioned above, there are new resonance signals detected at 19.17, 21.59, 25.19, and 48.45 ppm in the spectra of entries 9 and 10 (the norbornene contents up to 50%), which can be explained by the presence of norbornene dials and some NEN sequences next to norbornene microblocks. The intensity of the new signals increases with an increasing norbornene content in the copolymer. Surprisingly, the molecular weight distributions gradually decreased in the range 1.54 to 1.38, showing that higher monomer concentration makes for the process of the quasi-living copolymerization. Therefore, the **4d**/MMAO system indeed possesses some characteristics to promote the quasi-living copolymerization of ethylene with norbornene under suitable conditions.

We also studied the quasi-living nature of the copolymerizations of ethylene with norbornene promoted by the **4a**/MMAO system at long reaction time. Linear relationships between $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ and reaction time as well as narrow $\bar{M}_w/\bar{M}_n$ values for all the runs ($\bar{M}_w/\bar{M}_n$ = 1.07–1.23) were found for the **4a**/MMAO system (Figure 5). The GPC curves of the copolymers produced shifted to the higher molecular weight region with an increase of polymerization time, while the monomodal shape was retained. The results demonstrate that complex **4a** has a great potential for the quasi-living copolymerization of ethylene with norbornene.

D. The Preparation of Block Copolymer. The most important application of living polymerization is in block copolymerization. Because the same catalysts in this study can promote both the quasi-living polymerization of ethylene and the quasi-living copolymerization of ethylene with norbornene, we decided to synthesize block copolymer from ethylene and norbornene. The result is also collected in Table 3 (entry 11). Thus, ethylene gas was introduced to toluene in a reactor. After 5 min, the ethylene gas feed was stopped and the system was kept under nitrogen atmosphere for 5 min. Complex **4a** and MMAO were added to the reactor to prepare a polyethylene (PE) segment. After 5 min, norbornene was added and the ethylene gas feed was initiated at the same time to produce a sequential poly(ethylene-*co*-norbornene) segment for 5 min. As shown in Figure 6, the monomodal GPC curves for the PE A block ($\bar{M}_n = 9.6 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.30$) and the final A–B diblock ($\bar{M}_n = 14.3 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.38$) indicate a shift toward higher molecular weight range, while a narrow molecular weight distribution is retained, demonstrating the creation of a new A–B diblock polymer consisting of crystalline and amorphous segments, polyethylene-*b*-poly(ethylene-*co*-norbornene). The block copolymer possesses a norbornene content of 11.1 mol % (from NMR analysis), and the T_m value is 137 °C. A ^{13}C NMR spectrum of the resulting block copolymer supported its assignment as polyethylene and an alternating copolymer of ethylene with norbornene. This is a rare example of block copolymerization of ethylene and norbornene conducted at room temperature.

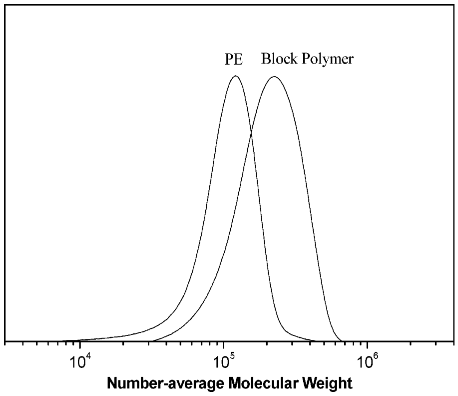

Figure 6. GPC profiles of block copolymer obtained by the **4a**/MMAO system.

Conclusion

A series of new titanium complexes with two nonsymmetric bidentate β-enaminoketonato ligands (**4a**–**e**) have been synthesized and characterized. The complexes **4a**–**e** are efficient catalysts for ethylene polymerization with MMAO as a cocatalyst at room temperature under atmospheric pressure. Moreover, the **4a**–**b**/MMAO catalyst systems display high activities (0.68–1.32 kg polymer/mmol cat·h) and produce high molecular weight polyethylenes ($\bar{M}_n > 5.0 \times 10^4$) with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.34$) as well as linear structures. The **4a**–**d**/MMAO catalyst systems, with high activities (0.5–3.2 kg polymer/mmol cat·h), are also capable of promoting the quasi-living copolymerization of ethylene with norbornene at room temperature to produce high molecular weight copolymers ($\bar{M}_n > 1.5 \times 10^5$) with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.35$). The essentially alternating copolymers, containing about 35.3–55.4 mol % norbornene, have been produced. This catalyst system is used for the synthesis of a new polyethylene-*b*-poly(ethylene-*co*-norbornene) diblock copolymer previously unavailable from Ziegler–Natta catalysts.

Experimental Section

General Comments. All manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere by means of standard Schlenk techniques. The NMR data of the polyethylenes and the ethylene/norbornene copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135 and 120 °C, respectively, with o-$C_6D_4Cl_2$

as the solvent. The other NMR data of the ligands and the complexes were obtained on a Varian Unity-300 MHz spectrometer at ambient temperature, with $CDCl_3$ as the solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. The molecular weight and the polydispersitiy of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Anhydrous diethyl ether, *n*-hexane, and toluene were refluxed and distilled from sodium/benzophenone under dry nitrogen. Dichlorobenzene was dried over CaH_2 and distilled before use. Norbornene was purchased from Aldrich, dried over sodium, vacuum-transferred, and degassed by repeated freeze−pump−thaw cycles. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. The *n*-butyllithium solution in hexane was purchased from Aldrich. 4,4,4-Trifluoro-1-phenyl-1,3-butanedione, 1,1,1-trifluoro-2,4-pentanedione, 1-benzoylacetone, 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione, and 4,4,4-trifluoro-1-thenoyl-1,3-butanedione were purchased from Aldrich.

Ligand and Complex Synthesis. (Ph)NC(CF_3)C(H)C(Ph)OH (2a). To a stirred solution of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (5.0 g, 23.0 mmol) in dried methanol (15.0 mL) were added aniline (4.3 g, 46.0 mmol) and formic acid (1.0 mL) as a catalyst. The mixture was refluxed and stirred for 48 h. During the stirring period, a yellow solution was formed. Evaporation of the methanol gave a reddish-black oil. The crude product was purified by column chromatography on silica gel with petroleum ether−ethyl acetate (100:1) as the eluent, affording compound **2a** (4.2 g, 15.0 mmol) as a yellow oil in 66.7% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 12.40 (s, 1H, O-H), 8.01−7.98 (dd, 2H, Ph-H), 7.59−7.49 (tt, 3H, Ph-H), 7.44−7.29 (m, 5H, Ph-H), 6.48 (s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.31 (imine C), 148.67, 148.26, 138.57, 137.72, 132.29, 128.96, 128.57, 127.42, 127.03, 125.93, 123.97, 121.94, 118.26 (Ph-C), 91.82 (=C). Anal. Calcd for $C_{16}H_{12}F_3NO$: C, 65.98; H, 4.15; N, 4.81. Found: C, 66.28; H, 4.13; N, 4.78.

(Ph)NC(CF_3)C(H)C(2-C_4H_3S)OH (2b). Compound **2b** was prepared via a procedure similar to that for **2a** as a yellow solid in 73.5% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 11.93 (s, 1H, O−H), 7.64−7.63 (d, 1H, thenoyl-H), 7.53−7.52 (d, 1H, thenoyl-H), 7.31−7.14 (m, 5H, Ph-H), 7.07−7.04 (t, 1H, thenoyl-H, 6.20 (s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 183.80 (imine C), 148.08, 147.66, 145.39, 137.62, 132.66, 129.93, 128.89, 128.10, 126.92, 125.74, 121.78, 118.10 (Ph-C and thenoyl-C), 92.00 (=C). Anal. Calcd for $C_{14}H_{10}F_3NOS$: C, 56.56; H, 3.39; N, 4.71. Found: C, 56.33; H, 3.35; N, 4.68.

(Ph)NC(CF_3)C(H)C(2-C_4H_3O)OH (2c). Compound **2c** was prepared via a procedure similar to that for **2a** as a yellow oil in 67.2% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 12.00 (s, 1H, O-H), 7.59−7.588 (t, 1H, furyl-H), 7.40−7.06 (m, 6H, Ph-H and furyl-H), 6.57−6.53 (m, 1H, furyl-H), 6.35 (s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 179.91(imine C), 153.22, 148.88, 148.46, 145.72, 137.64, 128.92, 126.99, 125.84, 121.75, 118.07, 115.39, 112.39 (Ph-C and furyl-C), 91.80 (=C). Anal. Calcd for $C_{14}H_{10}F_3NO_2$: C, 59.79; H, 3.58; N, 4.98. Found: C, 59.62; H, 3.56; N, 5.01.

(Ph)NC(CH_3)C(H)C(CF_3)OH (2d). Compound **2d** was prepared via a procedure similar to that for **2a** and separated out from solvent after cooling as a colorless crystal in 41.0% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 12.63 (s, 1H, O-H), 7.50−7.19 (m, 5H, Ph-H), 5.58 (s, 1H, =CH), 2.15 (s, 3H, −CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.41(imine C), 145.44, 132.02, 129.23, 123.53 (Ph-C), 89.49 (=C), 19.57 (CH_3-C). Anal. Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.40; N, 6.11. Found: C, 57.73; H, 4.37; N, 6.08.

(Ph)NC(Ph)C(H)C(CH_3)OH (2e). Compound **2e** was prepared via a procedure similar to that for **2d** as light yellow crystals in 80.0% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 13.10 (s, 1H, O-H), 7.93−7.91 (dd, 2H, Ph-H), 7.46−7.18 (m, 8H, Ph-H), 5.90 (s, 1H, =CH), 2.16 (s, 3H, −CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 188.43 (imine C), 161.99, 139.83, 138.45, 130.71, 128.97, 128.10, 126.89, 125.55, 124.49 (Ph-C), 94.10 (=C), 20.21 (CH_3-C). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.16; H, 6.40; N, 5.93.

[(Ph)NC(CF_3)C(H)C(Ph)O]$_2$TiCl$_2$ (4a). To a stirred solution of compound **2a** (1.0 g, 3.6 mmol) in dried diethyl ether (20.0 mL) at −78 °C was added a 1.60 M *n*-butyllithium hexane solution (2.4 mL, 3.8 mmol) dropwise over a 5 min period. The mixture was allowed to warm to room temperature and stirred for 2.5 h. The resulting mixture was added dropwise to $TiCl_4$ (0.2 mL, 1.8 mmol) in dried diethyl ether (20.0 mL) at −78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature and stirred for 16 h. The evaporation of the solvent in a vacuum yielded a crude product. To the crude product was added dried CH_2Cl_2 (20.0 mL), and the mixture was stirred for 10 min and then filtered. The filtrate was evaporated in a vacuum to afford a solid residue. Dried diethyl ether (3.0 mL) and dried *n*-hexane (20.0 mL) were added to the solid residue, and the mixture was stirred for 10 min. The filtration of the mixture gave complex **4a** as a black solid in 81.1% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.70 (d, 2H, Ph-H), 7.58 (d, 4H, Ph-H), 7.14 (m, 4H, Ph-H), 7.03 (m, 4H, Ph-H), 6.85 (m, 4H, Ph-H), 6.55 (m, 4H, Ph-H and =CH). Anal. Calcd for $C_{32}H_{22}Cl_2F_6N_2O_2Ti$: C, 54.96; H, 3.17; N, 4.01. Found: C, 54.86; H, 3.15; N, 4.04.

[(Ph)NC(CF_3)C(H)C(2-C_4H_3S)O]$_2$TiCl$_2$ (4b). Complex **4b** was prepared via a procedure similar to that for complex **4a** as a black solid in 78.2% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.36 (d, 1H, thenoyl-H), 7.31−7.02 (m, 6H, thenoyl-H and Ph-H), 6.84 (m, 1H, thenoyl-H), 5.30 (s, 1H, =CH). Anal. Calcd for $C_{28}H_{18}Cl_2F_6N_2O_2S_2Ti$: C, 47.28; H, 2.55; N, 3.94. Found: C, 47.39; H, 2.52; N, 3.91.

[(Ph)NC(CF_3)C(H)C(2-C_4H_3O)O]$_2$TiCl$_2$ (4c). Complex **4c** was prepared via a procedure similar to that for **4a** as a black solid in 76.5% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.53 (d, 2H, furyl-H), 7.35 (d, 4H, furyl-H), 7.09 (m, 4H, Ph-H), 6.90 (dd, 4H, Ph-H), 6.80 (d, 2H, Ph-H), 6.50 (m, 2H, furyl-H), 6.38 (s, 2H, =CH). Anal. Calcd for $C_{28}H_{18}Cl_2F_6N_2O_4Ti$: C, 49.51; H, 2.67; N, 4.12. Found: C, 49.63; H, 2.65; N, 4.10.

[(Ph)NC(CH_3)C(H)C(CF_3)O]$_2$TiCl$_2$ (4d). Complex **4d** was prepared via a procedure similar to that for **4a** as a brown solid in 85.2% a yield. ^1H NMR (300 MHz, C_6D_6): δ 7.43 (t, 2H, Ph-H), 7.35 (t, 1H, Ph-H), 7.20 (d, 2H, Ph-H), 5.30 (s, 1H, =CH), 2.14 (s, 3H, −CH_3). Anal. Calcd for $C_{22}H_{18}Cl_2F_6N_2O_2Ti$: C, 45.94; H, 3.15; N, 4.87. Found: C, 44.81; H, 3.17; N, 4.84.

[(Ph)NC(Ph)C(H)C(CH_3)O]$_2$TiCl$_2$ (4e). Complex **4e** was prepared via a procedure similar to that for **4a** as a brown solid in 90.4% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.92 (d, 1H, Ph-H), 7.52−7.36 (m, 6H, Ph-H), 7.21 (t, 3H, Ph-H), 5.30 (s, 1H, =CH), 2.16, (s, 3H, −CH_3). Anal. Calcd for $C_{32}H_{28}Cl_2N_2O_2Ti$: C, 64.99; H, 4.77; N, 4.74. Found: C, 64.81; H, 4.74; N, 4.76.

Ethylene Polymerization. Ethylene polymerization was carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Toluene (100 mL) was introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at a prescribed polymerization temperature, and then the ethylene gas feed (100 L/h) was started. After 15 min, polymerization was initiated by the addition of a toluene solution of MMAO and then a toluene solution of one of the five complexes into the reactor with vigorous stirring (900 rpm). After a prescribed time, isobutyl alcohol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulting mixture was added to the acidic methanol (1 mL of concentrated HCl in 500 mL of methanol). The solid polyethylene was recovered by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

Postpolymerization Method. The postpolymerization method was carried out using the same type of equipment under atmospheric pressure. Toluene (100 mL) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The toluene was kept at 25 °C, and then the ethylene gas feed (100 L/h) was started. After 5 min, the ethylene gas feed was stopped and the toluene solution was kept under N_2 for 5 min. To the resulting toluene solution were added toluene solutions of MMAO (10 mmol) and complex **4a** (5 μmol) to start ethylene polymerization.

Entry 11 in Table 2. After 35 min, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. Polymer purification and isolation were performed using the same method as the general procedure.

Entry 12 in Table 2. After 65 min, the ethylene gas feed (100 L/h, which is larger than that used by Fujita, 20 L/h) was initiated to perform postpolymerization. After 2 min, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. Polymer purification and isolation were performed using the same method as described in the general procedure.

Ethylene/NB Copolymerization. The copolymerization was performed in a glass flask (150 mL) equipped with a mechanical stirrer. Toluene (80 mL) was introduced to the nitrogen-purged reactor and stirred at 600 rpm. The solvent was kept at the prescribed polymerization temperature, and then the prescribed amount of nornornene was charged into the reactor. Then the ethylene gas feed (100 L/h) was started. After 15 min, polymerization was initiated by the addition of a MMAO heptane solution and then a solution of complex **4a** in toluene into the reactor. The polymerization was quenched after the prescribed time by the addition of isobutyl alcohol (5 mL). The resulting mixture was added to the acidic methanol (1 mL concentrated of HCl in 500 mL of methanol). The copolymer was collected by filtration, washed with methanol, and then dried at 60 °C for 24 h in a vacuum.

Characterization. ^{13}C NMR. The norbornene content of the copolymers was calculated according to the formula established by Waymouth:[14]

$$\text{mol N \%} = \frac{200 I_4}{I_{\mathrm{CH_2}}}$$

where I_4 is observed intensity of C_4, and $I_{\mathrm{CH_2}}$ are the total peak areas containing C_5 and C_6 and methylene peaks centered around 30 ppm.

Polyethylene-*block*-poly(ethylene/norbornene). Toluene (100 mL) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The toluene was kept at 25 °C, and then the ethylene gas feed (100 L/h) was started. After 5 min, the ethylene gas feed was stopped and the toluene solution was kept under N_2 for 5 min. To the resulting toluene solution were added toluene solutions of MMAO (6 mmol) and complex **4a** (3 μmol) to produce the polyethylene (PE) segment. After 5 min, the norbornene (5.0 g) and the ethylene gas feed (100 L/h) were introduced to the reactor simultaneously. After 5 min, the ethylene gas feed was stopped, and *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. The resulting copolymer purification and isolation were performed using the same method as the general procedure.

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Supporting Information Available: Tables of X-ray data for complex **4a**, ^{13}C NMR spectra of polyethylene, ^{13}C NMR spectra of block copolymers, ^{13}C NMR spectra of copolymers (entries 4−10 in Table 3), and GPC analyses of copolymers, etc. This material is available free of charge via the Internet at http://pubs.acs.org.

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