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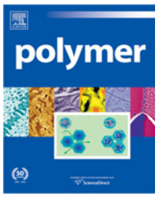

Synthesis, structure and ethylene (co)polymerization behavior of new nonbridged half-metallocene-type titanium complexes based on bidentate β-enaminoketonato ligands

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A series of novel half-metallocene-type titanium complexes $CpTiCl_2[PhN{=}C(R_2)CHC(R_1)O]$ (**2a**, R_1 = Cy, $R_2 = CF_3$; **2b**, R_1 = ^{t}Bu, $R_2 = CF_3$; **2c**, R_1 = Ph, $R_2 = CF_3$; **2d**, R_1 = Ph, $R_2 = CH_3$) have been synthesized by treating $CpTiCl_3$ with the corresponding bidentate β-enaminoketonato ligands $PhN{=}C(R_2)CHC(R_1)OH$ in the presence of triethylamine. Single crystal X-ray diffraction revealed that complex **2b** adopts distorted square-pyramid geometry around the titanium center. The complexes **2a**–**d** were investigated as the catalysts for ethylene polymerization and the copolymerization of ethylene with norbornene. All the complexes were active towards ethylene (co)polymerization in the presence of modified methylaluminoxane, and produced high molecular weight (co)polymers. The catalytic activity and the norbornene incorporation were highly dependent upon catalyst and reaction conditions employed. Among four complexes, **2c** exhibited both high catalytic activity and efficient norbornene incorporation under the same conditions, affording high molecular weight copolymers with unimodal molecular weight distributions.

1. Introduction

Over the past decades, an intense search has developed for well-defined, single-site transition metal olefin polymerization catalysts in both academic and industrial research laboratories. Group 4 metallocenes and related catalyst systems such as the half-sandwich amide (constrained-geometry catalysts) have been at the forefront of these developments [1,2]. Recently, nonbridged half-metallocene-type group 4 transition metal complexes of the type $CpM(L)X_2$ (Cp = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand; X = halogen, alkyl) become one of the promising candidates for new efficient catalysts for precise olefin polymerization because these complexes exhibited unique characteristics for ethylene (co)polymerizations [3–26]. For example, Sita and his coworkers utilized unsymmetrically substituted acetamidinate ligands derived from insertion of a carbodiimide into the metal methyl bond of Cp^RMMe_3 (M = /Ti, Zr) to produce chiral metal complexes that are active for the living stereoselective polymerization of 1-alkenes [13–15]. Nomura and his colleague demonstrated that the half-titanocenes containing an aryloxo ligand of the type, $Cp'TiCl_2(OAr)$ (OAr = aryloxy group), exhibited both high catalytic activities and efficient comonomer incorporations for the copolymerization of ethylene with α-olefin, styrene and norbornene, revealed that an efficient catalyst for desired polymerization can be simply modified by replacement of both the cyclopentadienyl and the anionic ancillary donor ligand [16–22]. Monocyclopentadienyl phenoxy-imine and phenoxy-amine complexes of group 4 transition metal were also synthesized and tested as the catalyst precursors for homo and copolymerization of ethylene with various comonomers [27–29].

We are interested in the design and synthesis of efficient transition metal catalysts for precise, controlled olefin polymerization. Previously, we reported the type of titanium catalysts chelating asymmetrical bidentate β-enaminoketonato ligands, $[PhN{=}C(R_2)CHC(R_1)O]_2TiCl_2$, and their use as the catalyst precursors for olefin polymerization [30–33]. 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 prepare novel nonbridged half-titanocene-type polymerization catalysts. Herein, we thus describe the synthesis and characterization of a number of the novel titanium complexes with cyclopentadienyl and β-enaminoketonato ligands (Scheme 1), and explore the potential application

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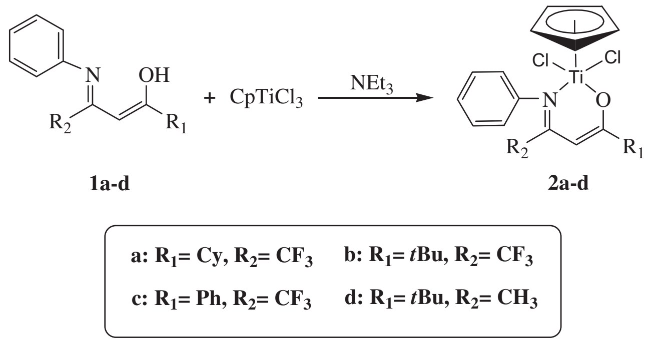


Scheme 1. Synthesis of half-titanocene complexes.

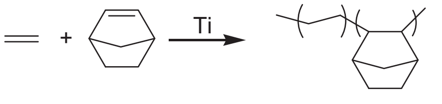
in ethylene polymerization and the copolymerization of ethylene with norbornene (Scheme 2). These catalysts display effective ability to copolymerize ethylene with norbornene and produce high molecular weight cyclic olefin copolymers.

2. Experimental

2.1. General procedures and materials

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glove box unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligands and complexes used were obtained on a Bruker 300 MHz spectrometer (300 MHz for ^{1}H, 75.5 MHz for ^{13}C) at ambient temperature, with $CDCl_3$ as the solvent (dried by MS 4 Å). The NMR data of the copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with *o*-$C_6D_4Cl_2$ as a solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc). The weight-average molecular weight (M_w) and the polydispersity index (PDI) of 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). The melting temperatures and glass transition temperatures of the copolymers were measured on a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C/min. The samples were first melted completely and then gradually cooled. The glass transition temperature (T_g) was determined on heating the sample again, typically from −50 to 350 °C.

Various β-enaminoketonato ligands containing different substituent on R_1 and R_2 positions, [PhN=C(R_2)CHC(R_1)OH] (**1a**, R_1 = Cy, R_2 = CF_3; **1b**, R_1 = ^{t}Bu, R_2 = CF_3; **1c**, R_1 = Ph, R_2 = CF_3; **1d**, R_1 = Ph, R_2 = CH_3) were prepared according to literature procedures [30]. Aniline and β-diketone derivatives for ligand synthesis and $CpTiCl_3$ and norbornene were purchased from Aldrich Chemical or Acros Organics, and used without further purification. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Commercial ethylene was directly used for polymerization without further purification.



Scheme 2. Copolymerization of ethylene with norbornene.

2.2. Synthesis of half-titanocene complexes

2.2.1. $CpTiCl_2[PhN{=}C(CF_3)C(H)C(Cy)O]$ (**2a**)

To a stirred solution of $CpTiCl_3$ (0.44 g, 2.0 mmol) in dried diethyl ether (20 mL) was added slowly a solution of PhN=C(CF_3)CHC(Cy)OH (0.60 g, 2.0 mmol) in diethyl ether (20 mL). The yellow reaction mixture was stirred for 10 min and Et_3N (0.3 mL, 216 mg, 2.1 mol) was added. After stiring for 4 h at room temperature the solution was concentrated to about 10 mL, and then the mixture was filtered to remove NH_4Cl. The chilled-concentrated *n*-hexane solution was placed in the freezer (−20 °C) and afforded complex **2a** (0.67 g, 70% yield) as red microcrystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12–1.51 (m, 6H, cyclohexyl), 1.81–2.04 (m, 4H, cyclohexyl), 2.55 (m, 1H, cyclohexyl), 6.03 (s, 1H, C*H*=C), 6.55 (s, 5H, C_5H_5), 7.31–7.42 (m, 5H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 25.8, 30.1, 46.2, 95.6, 117.3, 121.1, 124.5, 124.8, 127.2, 128.3, 150.0, 154.2, 192.5. EI-MS (70ev): m/z = 480 [M^+]. Anal. Calcd for $C_{21}H_{22}Cl_2F_3NOTi$: C 52.53; H 4.62; N 2.92. Found: C 52.59; H 4.58; N 2.88%.

2.2.2. $CpTiCl_2[PhN{=}C(CF_3)CHC(^tBu)O]$ (**2b**)

Synthesis of **2b** was performed according to the same procedure as that of **2a**, except that PhN=C(CF_3)CHC(^{t}Bu)OH (0.54 g, 2.0 mmol) was added slowly into a stirred diethyl ether solution containing $CpTiCl_3$ (0.44 g, 2.0 mmol) at −20 °C. The chilled solution (−20 °C) afforded red microcrystals (0.77 g, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 9H, ^{t}Bu), 6.18 (s, 1H, C*H*=C), 6.56 (s, 5H, C_5H_5), 7.19–7.42 (m, 5H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.8, 41.2, 94.8, 117.9, 121.7, 124.9, 125.4, 127.7, 128.8, 150.1, 155.0, 196.8. EI-MS (70ev): m/z = 454 [M^+]. Anal. Calcd for $C_{19}H_{20}Cl_2F_3NOTi$: C 50.25; H 4.44; N 3.08. Found: C 50.31; H 4.48; N 3.01%.

2.2.3. $CpTiCl_2[PhN{=}C(CF_3)CHCPhO]$ (**2c**)

Synthesis of **2c** was performed according to the same procedure as that of **2a**, except that PhN=C(CF_3)CHC(Ph)OH (0.58 g, 2.0 mmol) was added slowly into a stirred diethyl ether solution containing $CpTiCl_3$ (0.44 g, 2.0 mmol) at −20 °C. The chilled solution (−20 °C) afforded red microcrystals (0.76 g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.66 (s, 5H, C_5H_5), 6.73 (s, 1H, C*H*=C), 7.26–7.47 (m, 5H, aromatic), 7.51–7.59 (m, 3H, aromatic), 7.96–7.98 (m, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 95.3, 117.8, 121.6, 125.1, 127.8, 128.9, 129.3, 129.4, 133.2, 133.6, 150.6, 156.0, 179.6. EI-MS (70ev): m/z = 474 [M^+]. Anal. Calcd for $C_{21}H_{16}Cl_2F_3NOTi$: C 53.2; H 3.40; N 2.95. Found: C 53.14; H 3.47; N 3.02%.

2.2.4. $CpTiCl_2[PhN{=}C(CH_3)CHC(Ph)O]$ (**2d**)

Synthesis of **2d** was performed according to the same procedure as that of **1**, except that PhN=C(CH_3)CHC(Ph)OH (0.47 g, 2.0 mmol) was added slowly into a stirred diethyl ether solution containing $CpTiCl_3$ (0.44 g, 2.0 mmol) at −20 °C. The chilled solution (−20 °C) afforded red microcrystals (0.62 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (s, 3H, $-CH_3$), 6.33 (s, 1H, C*H*=C), 6.63 (s, 5H, C_5H_5), 7.31–7.90 (m, 10H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.3, 101.7, 124.1, 125.2, 127.1, 128.7, 129.1, 129.8, 132.2, 133.6, 153.1, 170.6, 173.5. EI-MS (70ev): m/z = 420 [M^+]. Anal. Calcd for $C_{21}H_{19}Cl_2NOTi$: C 60.03; H 4.56; N 3.33. Found: C 60.11; H 4.50; N 3.36%.

2.3. Copolymerization of ethylene with norbornene

A typical procedure was performed as follows: the prescribed amounts of toluene, norbornene and MMAO were added into the autoclave (100 mL, stainless steel) in the dry-box, and the apparatus was then purged with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of a toluene solution containing titanium complex. The polymerization was terminated with the addition of EtOH, and the resultant polymer was adequately washed with EtOH containing HCl and then dried under vacuum for several hours. The polymerization of ethylene was also performed in the same manner in the absence of norbornene.

2.4. Crystallographic studies

Single crystal of complex **2b** suitable for X-ray structure determination were grown from hexane solution at −20 °C in a glove box, thus maintaining a dry, O_2-free environment. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation (λ = 0.71073 Å). Lorentz, polarization factors were made for the intensity data and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

3. Results and discussion

3.1. Synthesis of new complexes $CpTiCl_2[PhN{=}C(R_2)CHC(R_1)O]$

Various half-titanocenes containing bidentate β-enaminoketonato ligands of the type $CpTiCl_2[PhN{=}C(R_2)CHC(R_1)O]$ (**2a**, R_1 = Cy, R_2 = CF_3; **2b**, R_1 = ^{t}Bu, R_2 = CF_3; **2c**, R_1 = Ph, R_2 = CF_3; **2d**, R_1 = Ph, R_2 = CH_3) were prepared in Et_2O by reaction of $CpTiCl_3$ with 1.0 equiv of corresponding ligands $PhN{=}C(R_2)CHC(R_1)OH$ in the presence of triethylamine, as shown in Scheme 1. These reactions took place along with evolution of hydrochloride, and the analytically pure samples were collected as red microcrystals in moderate to high yields (70–85%) from a concentrated dichloromethane solution layered with n-hexane at −30 °C. The resultant dichloro complexes (**2a**–**d**) were identified by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra of these complexes showed no complexity; a sharp single resonance assigned to the C_5H_5 protons at 6.54 ppm, a resonance ascribed to the methine proton (−CH=C−) at 6.03 ppm, as well as resonances corresponding to the ligand were observed. Integration of the ^{1}H NMR spectra of complexes **2a**–**d** confirms a 1:1 ratio of cyclopentadienyl to β-enaminoketonato ligand. The resultant complexes were also identified by elemental analyses. Crystals suitable for the crystallographic analysis were grown from the chilled-concentrated n-hexane solution containing **2b**, and the structures determined by X-ray crystallography as described below.

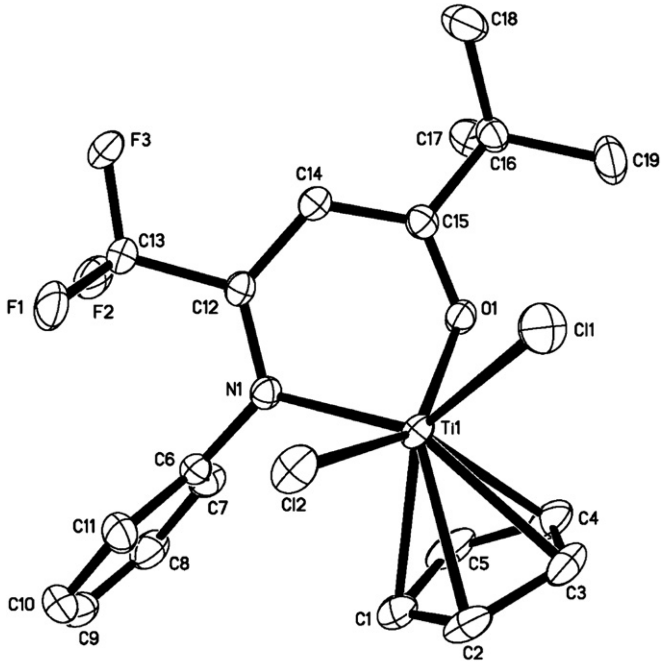


Fig. 1. Molecular structure of **2b**. Selected bond lengths (Å) and angles (°): Ti–O(1) = 1.9863(11), Ti–N(1) = 2.1322(13), Ti–Cl(1) = 2.3383(5), Ti–Cl(2) = 2.3409(5), O(1)–Ti(1)–N(1) = 78.99(4), O(1)–Ti(1)–Cl(1) = 83.39(4), N(1)–Ti(1)–Cl(1) = 133.26(4), O(1)–Ti(1)–Cl(2) = 142.96(3), N(1)–Ti(1)–Cl(2) = 82.57(4), Cl(1)–Ti(1)–Cl(2) = 86.35(2).

Compared with $CpTiCl_2[O\text{-}2\text{-}t\text{-}Bu\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)N{=}CH\}C_6H_3]$ (**3a**), in which the asymmetric unit consisted of two virtually identical molecules, β-enaminoketonato metal complex **2b** only showed one molecule in the solid state [28]. The structure and the selected bond distances as well as the angles for **2b** were shown in Fig. 1. **2b** folds a distorted square-pyramid geometry. The imino-nitrogen was coordinated to Ti, and the Ti–N bond distance in **2b** (2.132(13)) is shorter than those in complex **3a** (2.268(4) and 2.262 (3)). The Ti–Cp distance at 2.053 Å is normal and compares well

Table 1
Ethylene homopolymerization and ethylene/norbornene copolymerization by **2a**–**d**/MMAO catalytic systems.[a]

Entry	Catalyst (μmol)	NBE (mol/L)	Yield (mg)	Activity ($kg/mol_{Ti}\cdot h$)	M_w[b] (kg/mol)	M_w/M_n[b]	Mono Incorp. (%)[c]	T_g[d] (°C)	T_m[d] (°C)
1	**2a** (3.0)	0	80	160	272	2.38	–		135.4
2	**2a** (3.0)	0.2	200	400	378	2.85	1.9	n.d.[e]	120.7
3	**2a** (3.0)	1.0	90	180	375	2.54	10.9	−4.2	98.0
4	**2b** (3.0)	0	70	140	224	2.93	–		133.7
5	**2b** (3.0)	0.2	220	440	287	2.29	2.4	n.d.	118.1
6	**2b** (3.0)	1.0	Trace	–	–	–	–		
7	**2c** (3.0)	0	70	140	296	2.25	–		137.9
8	**2c** (3.0)	0.2	260	520	239	2.28	3.4	n.d.	116.0
9	**2c** (3.0)	1.0	120	240	315	2.37	20.1	30.8	92.2
10	**2d** (3.0)	0	Trace	–	–	–	–		
11	**2d** (3.0)	0.2	120	240	297	2.59	2.5	n.d.	118.2
12	**2d** (3.0)	1.0	170	340	354	2.02	9.6	−5.6	98.1

[a] Conditions: MMAO as cocatalyst, Al/Ti (molar ratio) = 1000, ethylene 4 atm, 25 °C, 10 min, V_{total} = 30 mL.
[b] Weight-average molecular weights and polydispersity indexes determined by high-temperature GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ vs narrow polystyrene standards.
[c] NBE incorporation (mol%) established by ^{13}C NMR spectra.
[d] Determined by DSC.
[e] None detected.

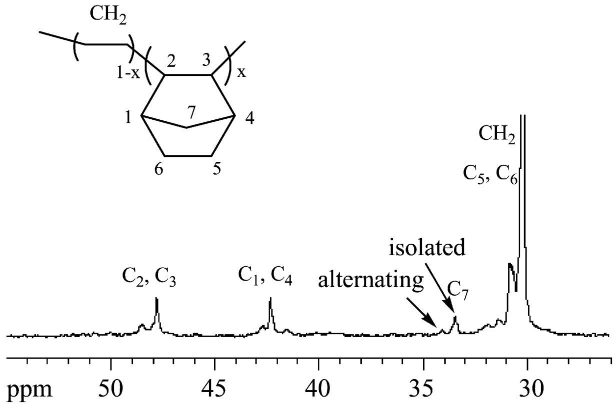


Fig. 2. ^{13}C NMR spectra (in 1,2,4-$C_6Cl_3H_3$ at 110 °C) for poly(ethylene-co-norbornene)s by **2c**-MAO catalyst systems (run 9).

with values observed in Ti(IV) η-cyclopentadienyl complexes [34]. The Ti–O bond distance in **2b** (1.969(3) Å) is slightly longer than those in **3a** (1.875(3) Å). The Cl–Ti–Cl angle of 86.35(5)° indicates slightly less steric congestion in the basal ligand. Attempts to prepare Cp*$TiCl_2$[PhN=C(R_2)CHC(R_1)O] complexes were unsuccessful, probably because of the increased steric bulk in metal center.

3.2. Ligand effects in ethylene polymerization and ethylene/norbornene copolymerization

Ethylene polymerizations by Cp$TiCl_2$[PhN=C(R_2)CHC(R_1)O] (**2a**–**d**) in the presence of MMAO were examined to explore the effect of the substituents of the β-enaminoketonato ligands on the catalytic activity (ethylene 4 atm, 25 °C, under the optimized Al/Ti molar ratio), and the results are summarized in Table 1. Complex **2a** showed moderate catalytic activity for ethylene polymerization affording high molecular weight (M_W) polymers with unimodal molecular weight distributions (MWDs) (entry 1). Both the catalytic activities and MWs for ethylene polymerization by **2b** and **2c** were similar to those by **2a**. However, complex **2d** showed negligible catalytic activity under the same conditions. One probable reason for explaining the fact would be that placement of appropriate electron withdrawing group in R_2 position maybe required for repeated ethylene coordination/insertion. The polymers prepared by **2a**–**c** were linear polyethylene, confirmed by ^{13}C NMR spectra and possessed relatively high molecular weights with unimodal MWDs. The M_W value for the resultant PE prepared by **2b** was lower than those by **2a** and **2c** maybe due to the steric effect of the substituent in R_2 position of the ligands (entry 4 vs entries 1 and 7).

We previously demonstrated that the titanium complexes containing bidentate β-enaminoketonato ligands were efficient catalyst precursors for ethylene/norbornene and its derivatives copolymerization in the presence of MMAO, and the catalytic activity and comonomer incorporation efficiency can be tuned by modifying the substituents in the ligands [31]. Herein, we thus explored ethylene/norbornene copolymerization by these nonbridged half-titanium complexes **2a**–**d**.

Ethylene undergoes facile copolymerization with norbornene in toluene under the different conditions. The typical data for the copolymerizations are also summarized in Table 1. It was revealed that the copolymerization with norbornene by complex **2a** took place, and the observed activity calculated on the basis of the polymer yield was higher than ethylene polymerization under low norbornene concentration (entries 1 and 2). The catalytic activity of complex **2a** decreased upon increasing the norbornene concentration (entries 2–3). The resultant products were poly(ethylene-*co*-norbornene)s confirmed by ^{13}C NMR spectra, and the copolymer possessed high molecular weight with unimodal molecular weight distributions as well as with uniform NBE distributions. These results suggest that the copolymerization took place with single catalytically active species. The MW values changed slightly upon increasing norbornene incorporation which increased linearly upon increasing norbornene/ethylene initial feed molar ratio. The same trend was seen in the copolymerization if analogue **2b** was employed. Interestingly, complex **2c** showed higher catalytic activity and norbornene incorporation than **2a** under the same conditions. The MW values for the resultant copolymers increased upon increasing norbornene incorporation whereas the M_w/M_n values were unchanged ($M_w/M_n = 2.28$–2.37), which suggests that resultant copolymer possessed uniform norbornene incorporation (entries 8–9). It is noteworthy that the catalytic activity of the analogues **2d** significantly increased in the presence of norbonrene, and the significant decreases in the catalytic activities by **2d** were not seen even under the high norbornene concentration (high initial norbornene/ethylene feed molar ratio) (entries 10–12). The efficiency of norbornene incorporation is at the same level as that by complex **2a** under the same conditions. These results clearly indicate that an efficient catalyst precursor for the ethylene copolymerization can be tuned to an efficient catalyst precursor for ethylene/norbornene copolymerization by modification of the anionic donor ligands. Taking into account these results, complex **2c** maybe best suited as the catalyst precursor for this copolymerization in terms of exhibiting a high catalytic activity with efficient norbornene incorporation.

The thermal properties of the resultant copolymers were analyzed by means of DSC thermograms. As expected, the melting temperature (T_m) of poly(E-co-NB)s declined, while the glass transition temperature (T_g) increased with increasing the content of NB. The copolymer containing 20.1 mol% of NB showed the T_g value at 30.8 °C (entry 9 in Table 1). ^{13}C NMR spectra for poly(ethylene-co-norbornene)s showed that the microstructures formed using **2a**–**d** possessed the isolated norbornene inserted unit among repeated ethylene insertions, and the alternating sequence was also present with low extent (Fig. 2). The peaks at 47.7, 42.2, and 33.5 are assigned to isolated syndiotactic C2/C3, C1/C4, and C7, respectively, and the peaks of 30.1–30.7 ppm are assigned to C5/C6 and short polyethylene sequences. It reveals the copolymer with lower than 10 mol % NB content predominantly consists of isolated NB units present in polyethylene chains. The appearance of the peaks at 48.4, 42.7, and 34.1 ppm in Fig. 2 are assigned to alternating isotactic C2/C3, C1/C4, and C7, respectively. The presence of the peaks at 33.5 ppm and absence of the peaks in the region of 36–37 ppm indicate the C7 is exo–exo but not endo–endo or endo–exo enchained [35]. No resonances ascribed to repeated norbornene insertion were observed, and the fact may clearly explain that negligible or no catalytic activity was observed in an attempted homopolymerization of norbornene by **2a**–**d**/MMAO catalytic systems.

4. Conclusions

We introduce a new family of Cp(L)TiX_2 catalysts, where L is β-enaminoketonato ligands. These half-titanocenes containing β-enaminoketonato ligands of the type Cp$TiCl_2$[PhN=C(R_2)CHC(R_1)O] can be easily synthesized by reaction of Cp$TiCl_3$ with the corresponding ligand in the presence of triethylamine. Molecular structures show that Ti atom is five-coordinate with the Cp ligand in the apical site of a distorted square-pyramid in the β-enaminoketonato complex. In the presence of MMAO, these nonbridged half-metallocene-type titanium complexes are active catalysts for ethylene polymerization at ambient temperature. The resultant polymers prepared by these complexes possessed high molecular weights with unimodal distributions, strongly suggesting that these polymerizations proceeded with a single catalytically active species without dissociation of the β-enaminoketonato ligand. Norbornene was tested for the copolymerization with ethylene in the presence of the half-titanium complexes containing β-enaminoketonato ligands. The observed effect of substituents in the ligands for the copolymerization with norbornene should be promising because the results clearly demonstrate that the efficient catalyst precursors for the desired (co)polymerization can be tuned by modification of the ligand structures. We believe that the results through this study would introduce important information for designing efficient transition metal catalysts for the desired (co)polymerization.

Acknowledgements

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Appendix. Supplementary information

Crystal structure for **2b** was shown in Supporting Information. Supplementary information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.03.012.

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