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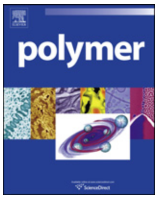

Novel bis(benzoin) titanium catalyst for homo- and copolymerization of norbornene with ethylene: Synthesis, characterization and catalytic properties

Hao Hu [a], Haiyang Gao [a], Keming Song [a], Fengshou Liu [a], Jieming Long [a], Ling Zhang [a], Fangming Zhu [a,b], Qing Wu [a,b,*]

[a] *Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, China*
[b] *PCFM Laboratory, OFCM Institute, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, China*

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ABSTRACT

A novel titanium(IV) dimeric complex $[(OC(Ph)HC(Ph)O)TiCl(\mu\text{-}OCH(Ph)C(Ph)(n\text{-}Bu)O)]_2$ (**1**) was synthesized and characterized, and its catalytic behaviors toward homo- and copolymerization of ethylene (E) and norbornene (NB) were also investigated. X-ray diffraction analysis of single crystal structure revealed that the titanium complex features a binuclear and six-coordinate, pseudo-octahedral geometry around titanium metal center with oxo-bridge in the solid state. Activated with methylalumoxane (MAO), the titanium complex exhibited good activities for the homopolymerizations of ethylene and norbornene with long lifetime and produced high-molecular weight linear PE and vinyl-type PNB, respectively. E–NB copolymers with high-molecular weight and high NB incorporation content could be also obtained by this catalyst. The incorporation of NB in the E–NB copolymers could be controlled by varying monomer ratio and reaction temperature. ^{13}C NMR analyses showed that the microstructures of the E–NB copolymers are predominantly alternated and isolated NB units, but the dyad and triad sequences of NB unit could be detected in the copolymers with high NB incorporation. The monomer reactivity ratios of the copolymerization were measured to be $r_E = 6.0$, $r_N = 0.05$ at 30 °C.

1. Introduction

Electronegative π-donor ligands such as aryloxides/alkoxides are attractive because they offer strong metal oxygen bonds that are expected to stabilize complexes of the electropositive metals [1]. Aryloxides with bulky substituents in positions 2 and 6 have been largely used in order to enforce a mononuclear character for species based on large metals [2,3]. There were few reports on the synthesis of titanium complexes with bulky substituent aryloxide ligands and their catalytic behaviors for ethylene polymerization [4–6]. The electronegative alkoxide groups make the metal atoms highly prone to nucleophilic attack, which meet the requirements as precursors for catalytic applications. Pellecchia and co-workers reported that alkoxide achiral complexes of type $Ti(OBu)_4$ in the presence of MAO–$Al(Me)_3$ produced a mixture of isotactic (up to 80% isotacticity) and atactic polypropylene [7]. Recently, a $[(HOEt)Ti(\mu\text{-}OEt)OEt(Cl)_2]_2$ dimeric complex was found to react with MAO to be catalyst for the polymerization of propylene and ethylene. The lifetime of this catalyst is sufficiently long to allow an effective polymerization [8].

Introduction of heteroatom(s) (N, S) with additional donor functionalities into chelating multidentate alkoxide or aryloxide ligands can provide an increased stabilization of reactive, electron-deficient metal centers [9–12]. Well-characterized group 4 metal complexes with multidentate alkoxide or aryloxide ligand systems have been studied for the olefin polymerization, where they show relatively good activities [13–16].

E–NB copolymers (Cyclic Olefin Copolymers, COCs) have attracted much attention with remarkable properties, such as a relatively high glass transition temperature (T_g), excellent optical transparency and high refractive indices [17–19]. In fact, these properties can be controlled by varying monomer composition, sequence distribution, and the stereoregularity of norbornene units in the copolymers, which depend on the different structure of the catalyst employed. In this connection, a series of single-site catalysts, including metallocenes [20–23], half-sandwiched titanocene [24,25] and constrained-geometry catalysts [26–30] have been prepared over the decades for the production of COCs with well-defined architecture. Recently, progresses have been made in the field of non-metallocene titanium complexes as catalytic precursors for E–NB copolymerization [31–36]. In general, most of the highly active non-metallocene titanium

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[*] Corresponding author. Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, China. Fax: +86 20 84114033.

E-mail address: ceswuq@mail.sysu.edu.cn (Q. Wu).

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catalysts for E–NB copolymerization possess nitrogen atoms as neutral donors, while less attention has been paid to titanium catalysts with oxygen-containing ligands. There were a few reports on the synthesis of dichlorobis(β-diketonato)titanium complexes and their catalytic behavior for α-olefin polymerization [37–39].

Whereas, there was nearly no report on E–NB copolymerization using titanium alkoxide precatalyst except amino diolate-based titanium complexes reported by Sudhakar [16]. In comparison to aryloxides, the synthetic chemistry of alkoxide-based complexes proved to be much more complicated. This is inherent to the high tendency of the relatively more basic alkoxide ligands to act as bridging ligands, eventually resulting in highly agglomerized structures. This difficulty can be partly overcome by increasing the steric bulk of the –OR moieties [10]. In this contribution, the synthesis of a new alkoxyl titanium complex with a pair of chelating benzoin ligands and investigations of its catalytic properties on homo- and copolymerization of ethylene and norbornene are reported. In fact, this inexpensive, air-stable, and very easy to synthesize titanium precursor appears as a good candidate for E–NB copolymerization.

2. Experimental

2.1. General

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard vacuum-line, Schlenk or glove box techniques. Solvents were purified using standard procedures. Benzoin was recrystallized from ethanol before use. The *n*-butyllithium (*n*-BuLi) solution in hexane (2.57 M) was purchased from Aldrich. Norbornene (bicyclo[2.2.1] hept-2-ene; Acros) was purified by distillation over potassium and used as a solution in toluene. MAO was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with $Al_2(SO_4)_3 \cdot 18H_2O$ as the water source. Methylene chloride was distilled from calcium hydride, and hexane was distilled from P_2O_5 under nitrogen. Titanium tetrachloride was distilled prior to use. Other commercially available reagents were purchased and used without purification.

2.2. Measurement

Elemental analyses were performed on a Vario EL microanalyzer. Mass spectrum for the complex was measured on a Thremo LCQ DECA XP liquid chromatography–mass spectrometry using electrospray ionization (EI) with CH_3CN as fluent phase. ^{1}H NMR spectra were carried out on Mercury-plus 300 MHz NMR spectrometers at room temperature in $CDCl_3$ solution for the ligand and the complex. ^{1}H NMR spectrum of the PNB was recorded on Mercury-plus 300 MHz NMR spectrometers at 80 °C with *o*-dichlorobenzene-d_4 as the solvent. ^{13}C NMR spectra of the polymer samples were recorded on a Varian INOVA 500 MHz spectrometer in a 4:1 mixture of *o*-dichlorobenzene and *o*-dichlorobenzene-d_4 (2.5 mL) at 120 °C. Chemical shifts were referenced to *o*-dichlorobenzene-d_4 (130.52 ppm). The NB contents in the copolymer were calculated from the ^{13}C NMR spectra by the following equation [27]:

$$X_N = 1/3\left(I_{C_1/C_4} + I_{C_2/C_3} + 2I_{C_7}\right)\Big/ I_{CH_2} \quad (1)$$

where I_{C_1/C_4} is integral of signals between 37.0 and 44.0 ppm, I_{C_2/C_3} is integral of signals between 44.5 and 56.0 ppm, I_{C_7} is integral of signals between 33.0 and 36.5 ppm, and I_{CH_2} is integral of signals between 28.0 and 32.5 ppm.

The molecular weight and molecular weight distribution of the polymer samples were determined at 135 °C by a Waters Alliance GPC 2000 type high-temperature chromatograph. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration curve was established with polystyrene standards.

The molecular weight of the PE samples was estimated by viscosimetric analysis, and the intrinsic viscosity of the polymer samples was measured in decalin at 135 °C using an Ubbelohde viscosimeter. The Mark–Houwink constants were taken from the literature, and the viscosity-average molecular weights (M_v) were calculated using Eq. (2) for PE [40]

$$[\eta] = 6.2 \times 10^{-4} M_V^{0.7} \quad (2)$$

The monomer reactivity ratios of the E–NB copolymerization were measured according to the Fineman–Ross method [41]. Ethylene concentrations ([E]) in toluene can be calculated according to the Henry–Gesetz expression (3) [42]:

$$[E] = P_E H_0 \exp(\Delta H_L / RT) \quad (3)$$

where P_E is the ethylene pressure (atm), H_0 is the Henry coefficient (0.00175 mol L^{-1} atm^{-1}), ΔH_L is the enthalpy of solvation of ethylene in toluene (10742 cal mol^{-1}), R is the universal gas constant, and T is the solution temperature (K).

Crystal data obtained with the ω–2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The structure was solved using direct methods, while further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2.3. Synthesis of complex **1**

To a stirred solution of benzoin (1.12 g, 5.26 mmol) in toluene (60 mL) at −78 °C was added a 2.57 M *n*-BuLi hexane solution (3.07 mL, 7.89 mmol) dropwise over a 5 min period. The mixture was allowed to warm to room temperature slowly and stirred for 2.5 h. $TiCl_4$ (0.289 mL, 2.63 mmol) in toluene (30.0 mL) was dropped into the resulting mixture at −78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature slowly and stirred for 16 h. The evaporation of the solvent *in vacuo* yielded a crude product. Dried CH_2Cl_2 (40.0 mL) was added to the crude product, and the mixture was stirred for 10 min and then filtered. Solvent was removed from the precipitate via cannula filtration, and the residual purple solid was washed with *n*-hexane. Drying *in vacuo* produced the desired titanium complex. Yield: 78.4%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.82 (d, 2H), 7.55 (t, 1H), 7.46 (t, 2H), 7.31–7.37 (m, 5H), 7.14–7.20 (m, 5H), 6.79–6.87 (m, 5H), 6.53 (s, 1H, CH), 4.81 (s, 1H, CH), 2.35 (t, 2H), 1.25 (m, 2H), 0.88 (m, 2H), 0.42 (t, 3H). Anal. Calcd. for $C_{64}H_{62}Cl_2O_8Ti_2$: C, 68.28; H, 5.55. Found: C, 68.01; H, 5.43. EI-MS: $[M + CH_3CN + PhCH_3 + H]^+$ (*m*/*z* 1256.0), $[M + H]^+$ (*m*/*z* 1124.8), $[M - Cl]^+$ (*m*/*z* 1088.9).

2.4. Norbornene polymerization

In a typical procedure, the appropriate MAO solid was introduced into a 50 mL round-bottom glass flask placed in an oil bath at a prescribed temperature, and then the desired amount of NB and toluene was added via syringe. The polymerization was started by adding a catalyst precursor solution with a syringe and the reaction mixture was continuously stirred for an appropriate period at the polymerization temperature. Polymerizations were terminated by the addition of acidic ethanol (ethanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying under vacuum at 60 °C to a constant weight.

2.5. *Ethylene polymerization and ethylene–norbornene copolymerization*

A 50 mL round-bottom glass flask (for 0.05 MPa ethylene pressure) or 100 mL stainless steel autoclave (for 1.0 MPa ethylene pressure) was charged with toluene, prescribed amount of MAO and NB (for E–NB copolymerization) at initialization temperature. The system was maintained by continuously stirring for 5 min, and then the titanium complex solution was charged into the flask or the autoclave. The pressure was maintained by continuously feeding ethylene gas and the reaction was carried out for a certain time. Polymerizations were terminated by the addition of acidic ethanol (ethanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying under vacuum at 60 °C to a constant weight.

3. Results and discussion

3.1. *Synthesis and molecular structure of titanium complex **1***

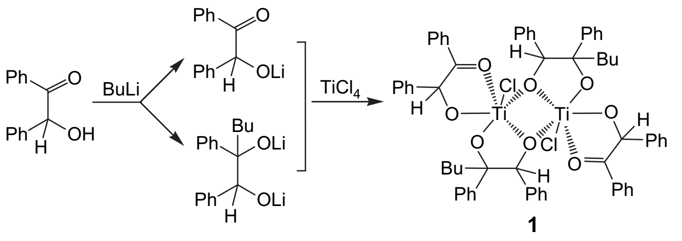
The synthetic route of the titanium complex is shown in Scheme 1. Benzoin was treated with 1.5 equivalents *n*-BuLi, and a mixture of two kinds of lithium salts of the corresponding benzoin was obtained. Reaction of the lithium salts with $TiCl_4$ in toluene gave titanium(IV) complex **1** in high yield (78.4%) as purple solids. The structure of complex **1** was fully characterized by ^1H NMR, EI-MS and elemental analysis (see Section 2). Crystal of complex **1** suitable for X-ray crystallography was grown from hexane/CH_2Cl_2 mixture solution. The crystallographic data, collection parameters, and refinement data are summarized in Table 1. ORTEP diagram is given in Fig. 1 [43].

Table 1
Crystallographic data for complex **1**

Empirical formula	$C_{64}H_{62}Cl_2O_8Ti_2$
F_W	1124.28
T (K)	173(2)
Crystal system	Monoclinic
Space group	*c*2/*c*
a (Å)	26.093(6)
b (Å)	14.638(4)
c (Å)	16.792(4)
α (°)	90
β (°)	118.072(4)
γ (°)	90
V (Å^3)	5659(2)
Z	4
D_{calc} (mg/m^3)	1.405
Absorption coefficient (mm^{-1})	0.528
F(000)	2488
θ range (°)	1.65–26.03
Reflections collected	15,190
Unique reflections	5541
Completeness to θ (%)	99.2 ($\theta = 26.03$)
Data/restraints/parameters	5541/0/343
Goodness-of-fit on F^2	0.967
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0778$, $wR_2 = 0.1997$
Largest difference in peak and hole (e Å^{-3})	0.841 and −0.404

Complex **1** in the solid state is dimeric with oxo-bridge; both metals are pseudo-octahedral geometry and related by an inversion center. Each titanium atom with a valency of four is surrounded by five O atoms and a terminal Cl ligand. The [O1, C1, C8, O2, Ti1] chelate ring is a good plane, while [O3, C15, C22, O4, Ti1] chelate ring is slightly twisted plane and features a boat conformation due to butyl substituent. The complex exhibits five different Ti–O bond lengths corresponding to the different charges of the ligands, anionic alkoxides Ti(1)–O(1) = 1.832 and Ti(1)–O(4) = 1.822 Å, bridging anionic alkoxides Ti(1)–O(3) = 2.002 Å and Ti(1)–O(3)# = 2.011 Å, and coordinative carbonyl Ti(1)–O(2) = 2.200 Å. Besides, the bite angles (O–Ti–O) are also different. The bite angle of O1–Ti1–O2 is 74.18°, while the bite angle of O3–Ti1–O4 is 78.36°. The Ti–Ti distance of complex is over 3 Å, suggesting that there is no direct metal–metal interaction.

Titanium complex **1** has one chiral center at α-ketoalkoxy ligand and two chiral centers at dialkoxy ligand per one titanium center. The X-ray structure analysis suggests that complex **1** adopts the dialkoxy ligand configuration of *cis* H–*n*-Bu as a single isomer and an enantiomer of α-ketoalkoxy ligand coordinate to Ti with dialkoxy ligand in stereoselective manner. In solid state, two single enantiomers of the titanium complex aggregate in stereoselective manner as shown in Fig. 1. The ^1H NMR spectrum of complex **1** (see Fig. 2) displays two single sharp resonances for the methine protons of the α-ketoalkoxy and dialkoxy ligands at 6.53 and 4.81 ppm, indicating no isomer existing in $CHCl_3$ solution. A quantitative analysis of complex **1** in toluene solution with CH_3CN as fluent phase was carried out by EI-MS with each protonated molecular ion in the positive ion mode. The monitoring ions were as follows: $[M + CH_3CN + PhCH_3 + H]^+$ (*m*/*z* 1256.0), $[M + H]^+$ (*m*/*z* 1124.8), $[M - Cl]^+$ (*m*/*z* 1088.9). Based on the ^1H NMR spectrum and EI-MS spectrum of the complex, it can be concluded that no exchange of ligands or recombination of titanium complexes takes place and the complex retains its dimeric form in solution at room temperature.



Scheme 1. Synthesis of titanium complex **1**.

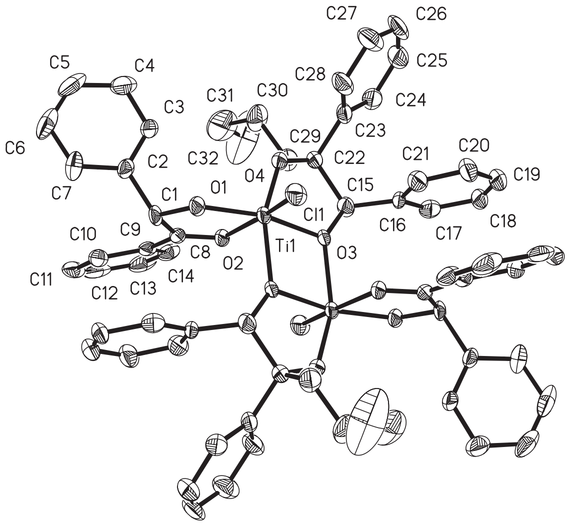


Fig. 1. Molecular structure of complex **1**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–Cl(1), 2.282(2); Ti(1)–O(1), 1.832(4); Ti(1)–O(2), 2.200(4); Ti(1)–O(3), 2.002(4); Ti(1)–O(4), 1.822(4); Ti(1)–O(3)#, 2.011(4); C(1)–O(1), 1.407(6); C(8)–O(2), 1.227(6); C(15)–O(3), 1.430(7); C(22)–O(4), 1.430(8); C(1)–C(8), 1.512(9); C(15)–C(22), 1.574(9); O(1)–Ti(1)–O(2), 74.81(17); O(4)–Ti(1)–O(3), 78.36(17); C(1)–O(1)–Ti(1), 127.6(4); C(8)–O(2)–Ti(1), 114.8(4); C(22)–O(4)–Ti(1), 125.5(4); C(15)–O(3)–Ti(1), 129.6(4); O(2)–Ti(1)–Cl(1), 168.33(13); O(1)–Ti(1)–Cl(1), 94.66(14); Ti(1)–O(3)–Ti(1)#, 108.33(17); O(3)–Ti(1)–O(3)#, 71.67(17); O(4)–Ti(1)–O(3)#, 148.72(18).

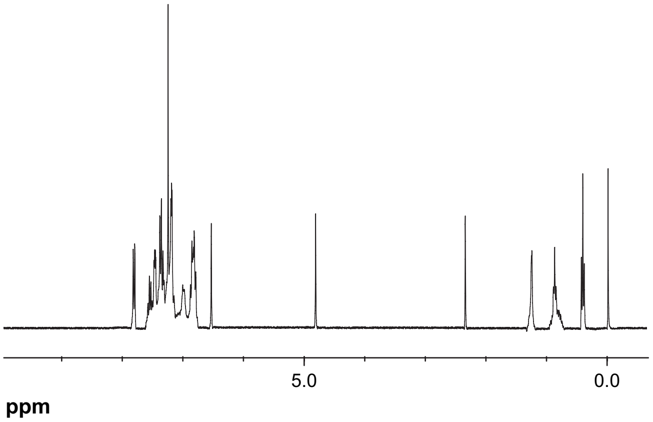


Fig. 2. ^{1}H NMR spectrum of complex **1** in $CDCl_3$ solution at room temperature using TMS as internal standard.

3.2. Ethylene polymerization

In the presence of MAO, titanium complex **1** was investigated as catalyst precursor for ethylene polymerization and the results are summarized in Table 2. It can be seen that at a constant Al/Ti ratio the catalytic activity increased with an increase of reaction temperature and reached a maximal value of 1.64×10^5 g mol^{-1} h^{-1} at 30 °C. This indicates that polymerization rate increased with an increase in temperature below 30 °C. An obvious decrease in catalytic activity was observed at higher temperatures, and this might be related to the thermal instability of the active species [44] and ethylene solubility in toluene [45] at higher temperatures The optimal temperature for each system depends on the balance between the propagation rate and the thermal instability.

Besides, it is also found that no induction period was observed for any of the ethylene polymerization reaction, and the polymerization activity decreased slowly with an increased time, the catalyst still showed good catalytic activity for 3 h. This result indicates that the bis(benzoin) titanium catalyst had long lifetime. Similar results have been reported by Tang using supported metallocene catalysts [46].

^{13}C NMR analysis of the obtained PEs shows only one peak at 30.0 ppm, and no signals due to branching carbons can be observed (see Fig. 3). The melting points of the polymers measured by DSC are in the 130.7–136.3 °C region, indicating that the produced polymers possess linear structures with virtually no branching.

The poor solubility of the high-molecular weight linear PEs in trichlorobenzene made it difficult to analyze by GPC, thus the molecular weight was calculated from the viscosity determined by an Ubbelohde viscosimeter in decalin at 135 °C. The listed data indicate that the molecular weights of the obtained PEs are very high up to 10^6 g mol^{-1}, and decrease with the increase of polymerization temperature uniformly due to an increasing chain termination reaction rate [47]. The molecular weight of the PE is unchanged with polymerization time.

Table 2
Ethylene polymerization with complex **1**/MAO

Entry	Temp (°C)	Time (h)	Yield (g)	Activity (10^5 g mol^{-1} h^{-1})	M_v[a] (10^6 g mol^{-1})	T_m (°C)
1	10	1	0.90	1.01	1.42	136.3
2	30	1	1.46	1.64	1.00	135.0
3	50	1	1.02	1.14	0.55	130.7
4	30	2	2.42	1.36	1.02	134.6
5	30	3	2.96	1.11	1.04	134.4

Polymerization conditions: solvent, toluene; total volume, 34 mL; complex, 8.9 μmol; Al/Ti = 320; 1.0 MPa ethylene pressure.

[a] The intrinsic viscosity was measured in decalin at 135 °C.

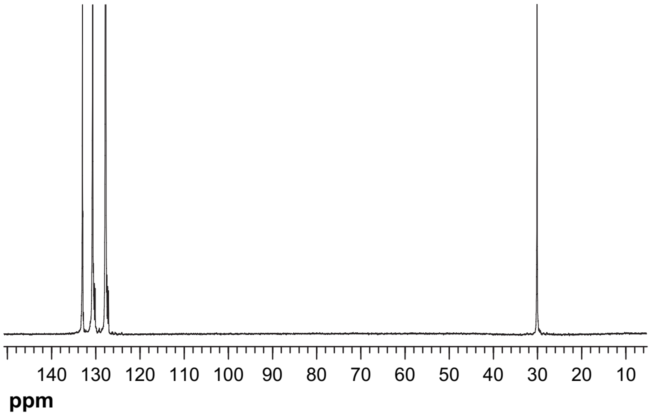


Fig. 3. ^{13}C NMR spectrum of PE obtained with complex **1**/MAO (Table 2, entry 2).

3.3. Norbornene polymerization

The NB polymerization was also carried out using **1**/MAO catalytic system, and the results are listed in Table 3. As reported in the literature, most of non-metallocene titanium complexes had no activity or showed low activities for NB polymerization [31,36], while complex **1** exhibited good activity for NB polymerization at 50 °C. With the increase of reaction temperature, the activity of complex **1** increased obviously and then decreased. At 50 °C, complex **1**/MAO showed the highest activity (3.58×10^5 g mol^{-1} h^{-1}). A higher temperature caused a decrease in the catalytic activity for NB polymerization because of the instability or decomposition of the active species [48]. Increasing the monomer concentration at fixed other reaction conditions resulted in dramatic increase in polymerization yield and activity. The obtained PNB is a white solid with poor solubility in common organic solvents [33]. The IR spectra of the obtained polymers reveal no traces of double bond which often appear at 1620–1680, 966, and 735 cm^{-1}, ensuring that the obtained products are vinylic addition polynorbornenes. The ^{1}H NMR spectrum of the obtained PNB further indicates that only vinyl addition polymerization occurs without any ROMP side reactions (see Fig. 4).

3.4. Ethylene–norbornene copolymerization

The performance of this catalyst system for E–NB copolymerization is shown in Table 4. It is found that bis(benzoin) titanium complex activated with MAO is an efficient catalyst for E–NB copolymerization, and the resultant copolymers prepared by complex **1**/MAO have high-molecular weights (M_w, 5.7–8.6×10^5 g mol^{-1}).

The copolymerization activity is affected by the quantities of charged NB at a constant E pressure. As the NB concentration increases (and thereby NB/E molar ratio increases), the catalytic activity decreases although the NB content in the copolymer

Table 3
Norbornene polymerization with complex **1**/MAO

Entry	Temp (°C)	NB (g)	Yield (g)	Activity (10^5 g mol^{-1} h^{-1})
6	10	4	0.02	0.02
7	30	4	0.13	0.15
8	50	4	1.55	1.74
9	70	4	0.27	0.30
10	30	2	Trace	–
11	30	8	0.97	1.09
12	50	8	3.19	3.58

Polymerization conditions: solvent, toluene; total volume, 34 mL; complex, 8.9 μmol; Al/Ti = 320; time, 1 h.

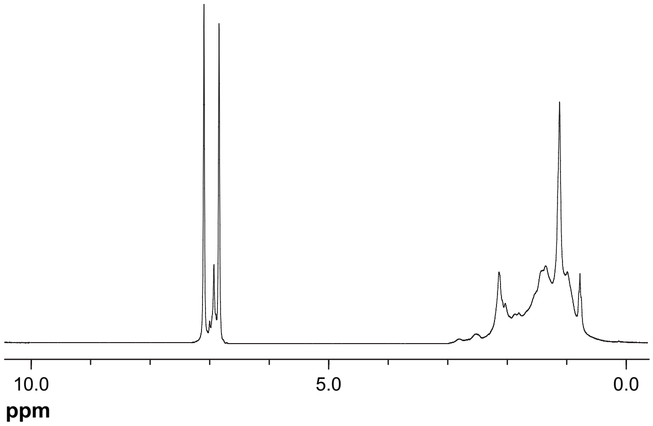


Fig. 4. ^{1}H NMR spectrum of PNB prepared by complex **1**/MAO (Table 3, entry 11).

increases and reaches a maximal value of about 50 mol%. Similar results were also reported for bis(pyrrolide-imine) titanium catalysts [31] and bis(β-diketiminato) titanium catalysts [36]. At high E pressure, complex **1**/MAO exhibits much higher activities and the copolymers with high-molecular weight and relatively low NB incorporation are obtained. The molecular weight distributions of the copolymers, which were determined by GPC measurement, are close to 2 and appear as a single modal in the GPC chromatograms, indicating that the copolymerizations occur on single active site. The active species as a heterobimetallic intermediate with oxo-bridge between titanium and aluminum atoms can be formed by reaction of complex **1** with MAO. Similar result has been confirmed by Eisen using a dichlorotitanium ethoxide complex as catalyst precursor [8]. For E–NB copolymerization, complex **1**/MAO also exhibits long lifetime and keeps high activity after 4 h.

Compared to copolymerization at 30 °C, the copolymerization at 50 °C has a higher activity and produces a copolymer with higher NB incorporation (comparing entry 16 with 15, and 21 with 17 in Table 4). As mentioned above, maximal activity of the NB polymerization appears at 50 °C, while that of the ethylene polymerization occurs at lower temperature. Therefore, high polymerization temperature can benefit NB monomer to compete in the copolymerization with ethylene monomer.

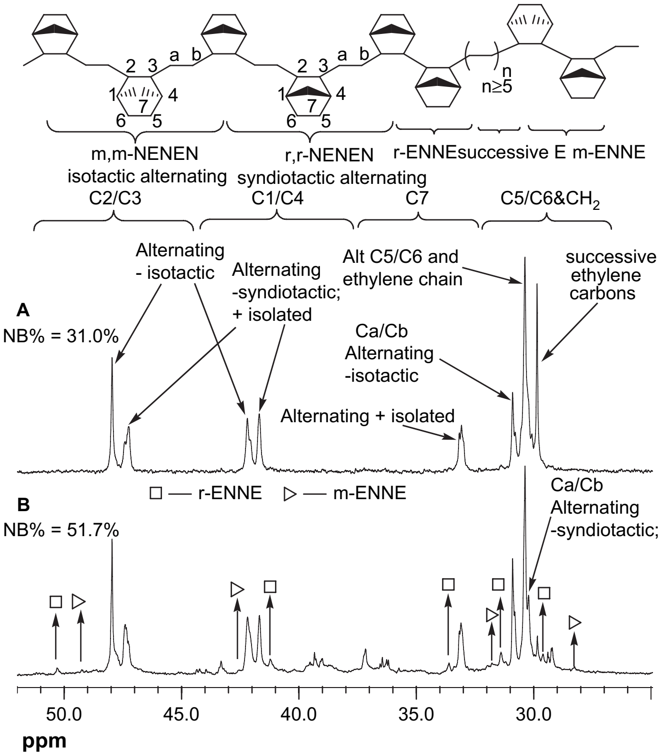


Fig. 5. ^{13}C NMR spectra of E–NB copolymers produced with complex **1**/MAO.

Microstructures of the E–NB copolymers obtained with complex **1**/MAO at different conditions were investigated by ^{13}C NMR spectra. The signals are assigned according to the previous literature [21,27,49]. As shown in Fig. 5A, the spectrum of the copolymer containing NB unit 31% displays only eight major peaks respectively at 29.9 ppm (successive E sequences), 30.4 ppm (isolated E + C_5/C_6), 30.9 ppm (C_5/C_6 + E sequence), 33.1 ppm (C_7), 41.7 and 42.2 ppm (C_1/C_4), 47.4 and 48.0 ppm (C_2/C_3), which are characteristics of the NB units existing as alternating (ENEN) and isolated (ENEE) sequences. The absence of resonances ranging from 35.0 to 41.0 ppm and below 29.9 ppm can exclude the possibility of NN dyad and NNN triad sequences [49].

Table 4
Ethylene–norbornene copolymerization with complex **1**/MAO

Entry	NB (g)	P_E (MPa)	Temp (°C)	Time (h)	Activity [a]	X_N[b] (%)	T_g/T_m (°C)	M_w[c] (10^5 g mol^{-1})	M_w/M_n[c]
13	2	0.05	30	1	0.27	29.2	61.5/	n.d.	n.d.
14	4	0.05	30	1	0.17	44.3	102.4/	n.d.	n.d.
15	8	0.05	30	1	0.13	48.4	113.3/	n.d.	n.d.
16	8	0.05	50	1	0.52	51.7	120.9/	n.d.	n.d.
17	8	1.0	30	1	2.56	24.8	44.9/	5.7	2.23
18	8	1.0	30	2	4.30	19.2	30.6/	6.6	1.87
19	8	1.0	30	3	3.18	18.9	/121.2	7.6	1.90
20	8	1.0	30	4	2.48	17.3	/120.3	8.6	1.99
21	8	1.0	50	1	7.80	38.2	n.d.	n.d.	n.d.
22	16	1.0	30	1	2.04	31.0	68.7/123.3	n.d.	n.d.
23	16	1.0	30	3	2.38	27.3	55.9/123.7	n.d.	n.d.
24	16	1.0	50	1	8.02	n.d.	n.d.	n.d.	n.d.

Polymerization conditions: solvent, toluene; total volume, 34 mL; complex, 8.9 μmol; Al/Ti = 320.

[a] Activity in 10^5 g mol^{-1} h^{-1}.

[b] Incorporated NB content in copolymer, calculated by ^{13}C NMR.

[c] Determined by GPC.

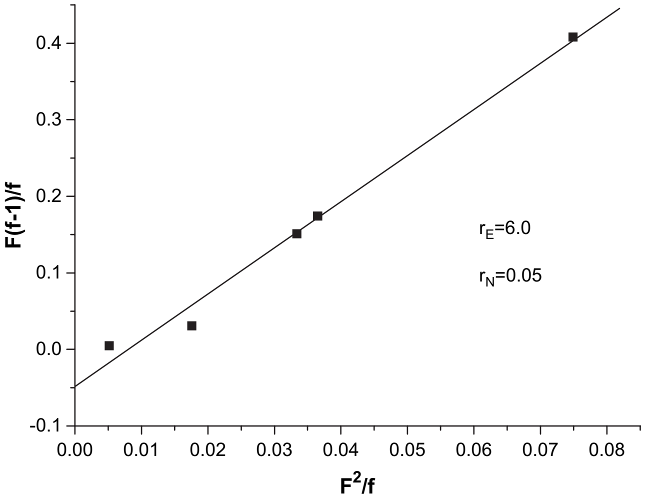


Fig. 6. Fineman–Ross plot for E–NB copolymerization with complex **1**/MAO at 30 °C (F = [E]/[NB] in feed, f = [E]/[NB] in copolymer).

Unlike E–NB copolymers obtained by bis(pyrrolide-imine) titanium [31] and bis(β-enaminoketonato) titanium catalysts [32] in which only alternating and isolated NB units were found, the E–NB copolymers with high NB contents obtained by **1**/MAO contain NN dyad and NNN triad sequences besides the alternating and isolated NB units. In the ^{13}C NMR spectrum of the E–NB copolymer with higher level of NB incorporation (NB% = 51.7 mol%), several additional signals assigned to the NN dyad and NNN triad sequences can

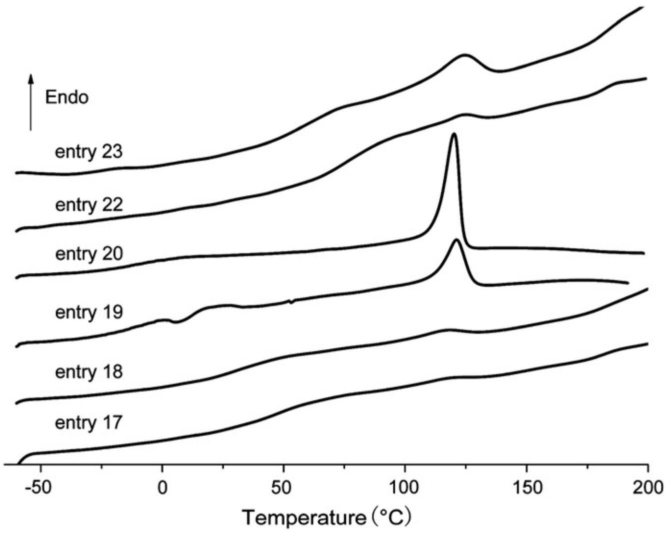


Fig. 7. DSC curves of E–NB copolymers prepared by complex **1**/MAO.

be observed in low intensity. According to the previous literature [50,51], the signals at 29.7, 31.4, 28.3, 31.7 ppm (C_5/C_6), 33.7 ppm (C_7), 41.2 and 42.7 ppm (C_1/C_4), 50.3 and 49.3 ppm (C_2/C_3) can be assigned to *racemic*- and *meso*-ENNE sequences. Otherwise, the signals assigned to NNN triad sequences appear at 29.0–29.6 ppm, 34.8–40.3 ppm and 43.3–44.3 ppm [23,24,52]. The existence of NN dyad and NNN triad sequences in the copolymers can be attributed to a high activity of NB homopolymerization by the catalyst.

The Fineman–Ross plot for the E–NB copolymerization performed at 30 °C is shown in Fig. 6. The monomer reactivity ratios are calculated to be $r_E = 6.0$ and $r_N = 0.05$. The larger value of r_N compared to the results from non-metallocene titanium catalyst system reported in the literature [33] indicates that the coordination and insertion velocity of NB are relatively high for **1**/MAO catalyst system.

As shown in Fig. 7, the DSC heating profiles of the copolymers exhibit different glass transition temperature (T_g) depending upon NB incorporation. The copolymers containing high NB incorporation show only a single T_g, while those containing low NB incorporation show simultaneously T_g and melting temperature (T_m). As shown in Fig. 8, there is a linear relationship between NB content in the copolymer and T_g. The copolymers containing low NB incorporation show the obvious melt peaks (*ca.* 120 °C), which can be a result of relative long ethylene sequences confirmed by ^{13}C NMR and WAXD analyses. Similar results have been reported in cycloolefin-based copolymers (COC) catalyzed by group IV metal catalysts [53–55]. For example, Kaminsky early reported ethylene–norbornene copolymer with 29% norbornene incorporated content at high monomer concentration ratio ($C_{NB}/C_E = 1608$) using $[Me_2Si(Ind)_2]ZrCl_2$/MAO catalytic system showed two signals in the DSC curve ($T_g = 38$ °C and $T_m = 123$ °C) [53]. At high NB contents, the copolymers should be amorphous and usually not show any evidence of melting endotherms [27,33]. The melting peak could be from some PE chains containing very lower NB contents because the copolymer structure was not uniform.

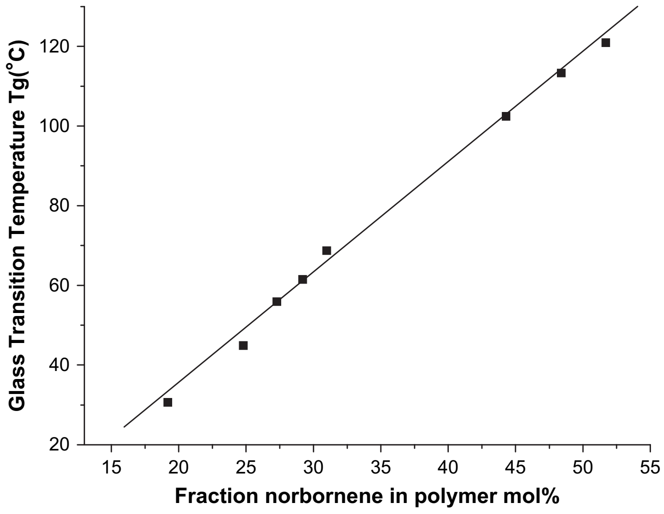


Fig. 8. Dependence of glass transition temperature (T_g) upon NB content.

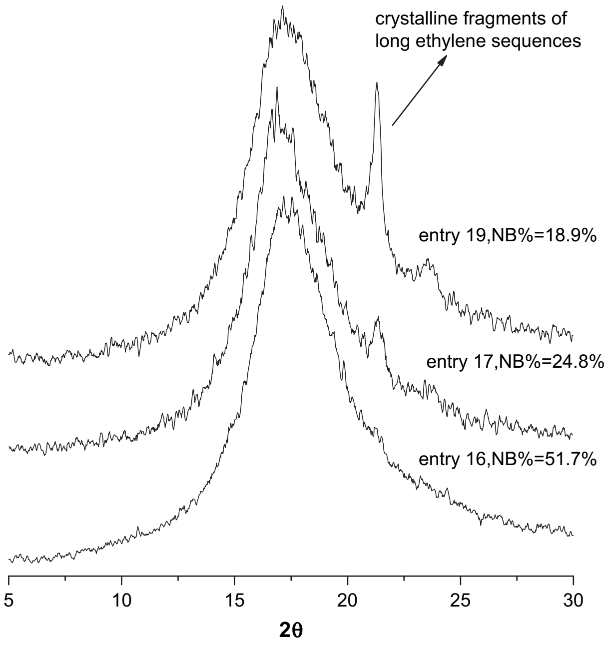


Fig. 9. WAXD diffractograms for E–NB copolymers obtained with complex **1**/MAO.

Fig. 9 shows WAXD diffractograms of the copolymers with different NB contents. For low NB content copolymers (NB ≤ 24.8%), two sharp peaks appear at 2θ of 21° and 24° characterized as PE crystal, indicating the existence of long E sequences. With the increase of NB content in the copolymers, the two peaks decreased that indicated the copolymers become completely amorphous state. This result is also consistent with ^{13}C NMR and DSC observations.

4. Conclusions

In summary, a new titanium complex with two benzoin ligands has been synthesized and characterized fully. In the presence of MAO, the titanium complex showed good activities for ethylene and norbornene polymerizations. The catalyst is also effective for E–NB copolymerization and produced random copolymer with high-molecular weight and NB content of 17–52%. ^{13}C NMR analyses showed the E–NB copolymers contained predominantly alternated and isolated NB units. Dyad and triad sequences of NB unit could be detected in the E–NB copolymer with high incorporated NB content. The T_g value of the copolymer increased with increasing the incorporated NB content.

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References

[1] Hubert-Pfalzgraf LG. Coord Chem Rev 1998;178–180:967.
[2] Linden A, Schaverien CJ, Meijboom N, Ganter C, Orpen AG. J Am Chem Soc 1995;117:3008.
[3] Firth AV, Stewart JC, Hoskin AJ, Stephan DW. J Organomet Chem 1999;591:185.
[4] Suzuki Y, Inoue Y, Tanaka H, Fujita T. Macromol Rapid Commun 2004;25:493.
[5] Sobota P, Przybylak K, Utko J, Jerzykiewicz LB, Pombeiro AJL, Guedes da Silva MFC. Chem—Eur J 2001;7:951.
[6] Frediani M, Sémeril D, Comucci A, Bettucci L, Frediani P, Rosi L, et al. Macromol Chem Phys 2007;208:938.
[7] Olivia L, Longo P, Pellecchia C. Macromol Chem Commun 1988;9:51.
[8] Gueta-Neyroud T, Tumanskii B, Kapon M, Eisen MS. Macromolecules 2007;40:5261.
[9] Mack H, Eisen MS. J Chem Soc Dalton Trans 1998:917.
[10] Lavanant L, Chou T-Y, Chi Y, Lehmann CW, Toupet L, Carpentier J-F. Organometallics 2004;23:5450.
[11] Shao PC, Gendron RAL, Berg DJ, Bushnell GW. Organometallics 2000;19:509.
[12] Gauvin RM, Osborn JA, Kress J. Organometallics 2000;19:2944.
[13] Fujita M, Seki Y, Miyatake T. J Polym Sci Part A Polym Chem 2004;42:1107.
[14] Janas Z, Jerzykiewicz LB, Sobota P, Szczegot K, Wioeniewska D. Organometallics 2005;24:3987.
[15] Lavanant L, Toupet L, Lehmann CW, Carpentier J-F. Organometallics 2005;24:5620.
[16] Sudhakar P. J Polym Sci Part A Polym Chem 2008;46:444.
[17] Cherdron H, Brekner M-J, Osan F. Angew Makromol Chem 1994;223:121.
[18] Kaminsky W, Engehause R, Kopf J. Angew Chem Int Ed 1995;34:2273.
[19] Rische T, Waddon AJ, Dickinson LC, MacKnight WJ. Macromolecules 1998;31:1871.
[20] Kaminsky W, Bark A, Arndt M. Makromol Chem Macromol Symp 1991;47:83.
[21] Ruchatz D, Fink G. Macromolecules 1998;31:4674.
[22] Lee BY, Kim YH, Won YC, Han JW, Suh WH, Lee IS, et al. Organometallics 2002;21:1500.
[23] Wendt RA, Fink G. J Mol Catal A Chem 2003;203:101.
[24] Nomura K, Tsubota M, Fujiki M. Macromolecules 2003;36:3797.
[25] Nomura K, Wang W, Fujiki M, Liu JY. Chem Commun 2006:2659.
[26] McKnight AL, Waymouth RM. Macromolecules 1999;32:2816.
[27] Hasan T, Ikeda T, Shiono T. Macromolecules 2004;37:8503.
[28] Naga N. J Polym Sci Part A Polym Chem 2005;43:1285.
[29] Ni JG, Lü CS, Zhang YT, Liu ZQ, Mu Y. Polymer 2008;49:211.
[30] Li HC, Li JC, Zhang YT, Mu Y. Polymer 2008;49:2839.
[31] Yoshida Y, Mohri J, Ishii S, Mitani M, Saito J, Matsui S, et al. J Am Chem Soc 2004;126:12023.
[32] Li XF, Dai K, Ye WP, Pan L, Li YS. Organometallics 2004;23:1223.
[33] Vijayakrishna K, Sundararajan G. Polymer 2006;47:8289.
[34] Zuo WW, Sun WH, Zhang S, Hao P, Shiga A. J Polym Sci Part A Polym Chem 2007;45:3415.
[35] Gao ML, Wang C, Sun XL, Qian CT, Ma Z, Bu SZ, et al. Macromol Rapid Commun 2007;28:1511.
[36] Li YF, Gao HY, Wu Q. J Polym Sci Part A Polym Chem 2008;46:93.
[37] Soga K, Kaji E, Uozumi T. J Polym Sci Part A Polym Chem 1997;35:823.
[38] Ahn C-H, Tahara M, Uozumi T, Jin J, Tsubaki S, Sano T, et al. Macromol Rapid Commun 2000;21:385.
[39] Shmulinson M, Galan-Fereres M, Lisovskii A, Nelkenbaum E, Semiat R, Eisen MS. Organometallics 2000;19:1208.
[40] Brandrup J, Immergut EH, Grulke EA. In: Abe A, Bloch DR, editors. Polymer handbook. 4th ed. New York: John Wiley & Sons; 1999.
[41] Fineman M, Ross SD. J Polym Sci 1950;5:259.
[42] Krauss VW, Gestrich W. Chem Technol 1977;6:513.
[43] Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 675849. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
[44] Sudhakar P, Amburose CV, Sundararajan G, Nethaji M. Organometallics 2004;23:4462.
[45] Gao HY, Ke ZF, Pei LX, Song KM, Wu Q. Polymer 2007;48:7249.
[46] Shi LY, Qin YX, Cheng WX, Chen H, Tang T. Polymer 2007;48:2481.
[47] Schilling M, Bal R, Görl C, Alt HG. Polymer 2007;48:7461.
[48] Gao HY, Pei LX, Li YF, Zhang JK, Wu Q. J Mol Catal A Chem 2008;280:81.
[49] Wendt RA, Mynott R, Hauschild K, Ruchatz D, Fink G. Macromol Chem Phys 1999;200:1340.
[50] Arndt-Rosenau M, Beulich I. Macromolecules 1999;32:7335.
[51] Wendt RA, Fink G. Macromol Chem Phys 2001;202:3490.
[52] Ruchatz D, Fink G. Macromolecules 1998;31:4669.
[53] Kaminsky W, Noll A. Polym Bull 1993;31:175.
[54] Lasarov H, Pakkanen TT. Macromol Rapid Commun 2001;22:434.
[55] Lasarov H, Mönkkönen K, Pakkanen TT. Macromol Chem Phys 1998;199:1939.