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Synthesis and structures of adamantyl-substituted constrained geometry cyclopentadienyl–phenoxytitanium complexes and their catalytic properties for olefin polymerization

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ABSTRACT

A number of new constrained geometry titanium complexes, [η^5: η^1-2-C_5Me_4-4-R-6-Ad-C_6H_2O]$TiCl_2$ [Ad = adamantyl, R = Me (**8**), ^{t}Bu (**9**)] and [η^5: η^1-$C_5H_2Ph_2$-4-^{t}Bu-6-Ad-C_6H_2O]$TiCl_2$ (**10**), were synthesized from reactions of $TiCl_4$ either directly with corresponding free ligands, 2-C_5Me_4H-4-R-6-Ad-C_6H_2OH [R = Me (**5**), ^{t}Bu (**6**)], or with the dilithium salt of the free ligand 2-$C_5H_3Ph_2$-4-^{t}Bu-6-Ad-C_6H_2OH (**7**). These new titanium complexes were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses, and the molecular structures of **8** and **9** were determined by single-crystal X-ray crystallography. Upon activation with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ (TIBA/B), these complexes exhibit high catalytic activity for 5-ethylidene-2-norbornene (ENB) polymerization as well as ethylene/1-hexene and ethylene/ENB copolymerization with good tacticity-control ability for the ENB polymerization and high comonomer incorporation ability for the copolymerization reactions. It was found that the bulky adamantyl substituent at the *ortho* position of the phenoxy group in the ligands of these complexes apparently influences the molecular weight and the microstructure of the resultant polymers.

1. Introduction

In the last two decades, the so-called constrained geometry metallocene catalysts (CGC) with the general formula of [η^5: η^1-$C_5R_4(SiMe_2)NR^1$]$TiCl_2$ (**I** in Chart 1) have been widely studied in academic [1–4] and industrial [5–8] institutions because of their high performance in catalyzing the copolymerization of different olefins. Various modifications on the chelating ligands have been made in order to improve the catalytic performance of the CGC catalysts through steric and electronic effects of their ligands. For example, a variety of CGC catalysts with ligands bearing different substituted cyclopentadienyl, indenyl and fluorenyl groups [9–14], different coordinating heteroatoms [15–25], and linkages [26–28] have been synthesized and studied. In comparison with the CGC catalysts of type **I**, the catalysts with a pendent oxygen donor on the cyclopentadienyl ring received relatively less attention and have not been studied systematically [3]. We and other groups have developed a number of CGC catalysts of the type [η^5: η^1-C_5Me_4-ArO]$TiCl_2$ (**II** in Chart 1) and found that these catalysts show high catalytic activity in ethylene/α-olefin copolymerization though they produce copolymers with relatively low molecular weights due probably to their ligands being not bulky enough [16–19]. In addition, this type of catalysts were found to show good catalytic properties in the copolymerization of ethylene with cyclo-olefins such as norbornene or 5-ethylidene-2-norbornene (ENB) and produce copolymers with relatively high molecular weights and comonomer incorporation [29,30]. To further improve the catalytic property of this type of catalysts, we have synthesized several new titanium complexes of type **II** bearing a bulky adamantyl substituent at the *ortho*-position of the phenoxy group in their ligands. It was found that these new complexes, upon activation with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ (TIBA/B), exhibit higher catalytic activity and produce polymers with higher molecular weights for ethylene/1-hexene (E/H) copolymerization, and show better comonomer incorporation ability in E/ENB copolymerization and higher tacticity-control ability in ENB polymerization than the known complexes of this type [30]. In this paper, we wish to report the synthesis and structural characterization of the new titanium complexes, [η^5: η^1-2-C_5Me_4-4-R-6-Ad-C_6H_2O]$TiCl_2$ [Ad = adamantyl, R = Me (**8**), ^{t}Bu (**9**)] and [η^5: η^1-2-$C_5H_2Ph_2$-4-^{t}Bu-6-Ad-C_6H_2O]$TiCl_2$ (**10**), as well as the results from the ENB polymerization, the E/H and E/ENB copolymerization catalyzed by these complexes in the presence of Al^iBu_3 and $Ph_3CB(C_6F_5)_4$.

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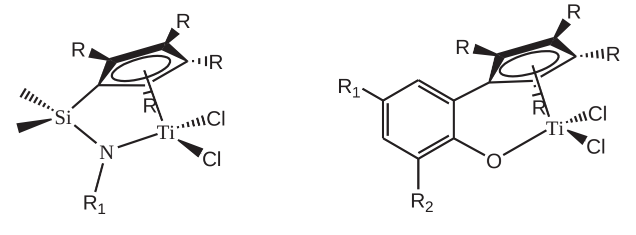
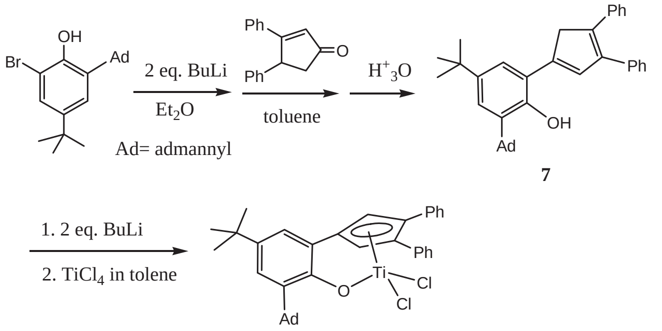


I

II

Chart 1.



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10

Scheme 2. Synthetic route of complex **10**.

2. Results and discussion

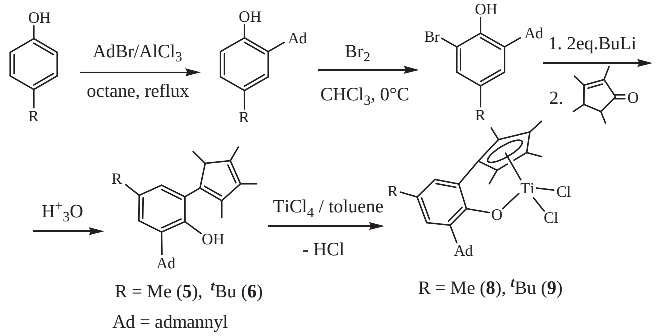
2.1. Synthesis of ligands and titanium complexes

The synthetic routes to complexes **8**, **9** and **10** are shown in Schemes 1 and 2, respectively. Reaction of 1-bromoadamantane with 1 equivalent of corresponding phenol catalyzed by $AlCl_3$ in octane at refluxing temperature gives 2-adamantyl-4-alkylphenol (**1**, or **2**) in 45–55% yields. Under similar conditions, compound **2** was synthesized in higher yields than compound **1**. Treatment of compound **1** or **2** with 1.05 equivalent of Br_2 in chloroform at 0 °C produces 2-bromo-4-alkyl-6-adamantylphenol (**3** or **4**) in about 90% yields. Following previously reported procedures [17,18], free ligands **5** and **6** were synthesized in relatively high yields (45–50%) by the reaction of tetramethylcyclopentenone with the corresponding dilithium phenoxide, while ligand **7** was synthesized in low yields (35–40%) with diphenylcyclopentenone, instead of tetramethylcyclopentenone, as the starting material. Compounds **1**–**7** were all characterized by ^1H NMR and elemental analyses.

Titanium complexes **8** and **9** were synthesized in high yields (80–90%) by the direct HCl elimination reaction between $TiCl_4$ and a corresponding free ligand (**5** or **6**) in the way reported previously [16]. This synthetic method was found to work much better for the synthesis of complexes of this type in comparison to other synthetic approaches such as amine elimination [31–33], alkane elimination [34,35], and Me_3SiCl elimination reactions [36–38]. However, attempts to synthesize complex **10** by this method were unsuccessful due probably to that the coordination of the phenyl groups on the cyclopentadiene ring of the free ligand **7** reduces the chance for the cyclopentadiene ring to coordinate to the titanium atom and therefore makes the HCl elimination reaction between TCl_4 and the cyclopentadiene ring difficult. The Me_3SiCl elimination reaction was also found to be inefficient for the synthesis of complex **10**. Finally, complex **10** was synthesized by the traditional lithium salt elimination reaction as shown in Scheme 2. All three titanium complexes **8**–**10** were characterized by ^1H, ^{13}C NMR and elemental analyses. The ^1H and ^{13}C NMR spectra of **8**–**10** indicate that they all have C_s-symmetric structures in solution.

2.2. Crystal structures of 8 and 9

The molecular structures of complexes **8** and **9** were further confirmed by single-crystal X-ray analysis. The ORTEP drawings of the molecular structures of **8** and **9** are shown in Figs. 1 and 2, respectively. The selected bond lengths and angles are summarized in Table 1. The general structural features of **8** and **9** are comparable to those previously reported for complexes **I** and **II**. Both molecules possess C_s-symmetry with a distorted octahedral coordination environment in their solid state structures and adopt a three-legged piano stool geometry with the phenoxy O atom and the two Cl atoms being the three legs and the Cp ring being the seat. The Cp(cent)–Ti–O angles for **8** and **9** are 106.5°, 106.7°, respectively, which are slightly smaller than those of known complexes **II** (106.8–107.3°) [17] and that of the Cp(cent)–Ti–N angle in complex [η^5: η^1-$C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (107.6°) [15], indicating that complexes **8** and **9**, as potential olefin copolymerization catalyst precursors, possess similar sterically open features to complexes **I** and known complexes **II**. The C(Cp)–C(phenolate) vector is bent 11.9° in **8** and 11.0° in **9** from the Cp ring plane, being similar to those for the known complexes **II** (9.9–11.3°) [17] and reflecting similar steric strain in these complexes in the solid state. The Ti–C(Cp) (av) distances of 2.011 Å in **8** and 2.007 Å in **9** are



Scheme 1. Synthetic route of complexes **8** and **9**.

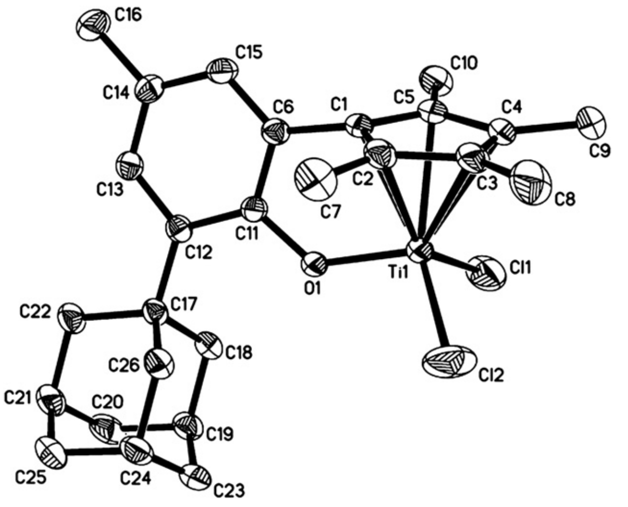


Fig. 1. Structure of complex **8** (thermal ellipsoids are drawn at the 30% probability level).

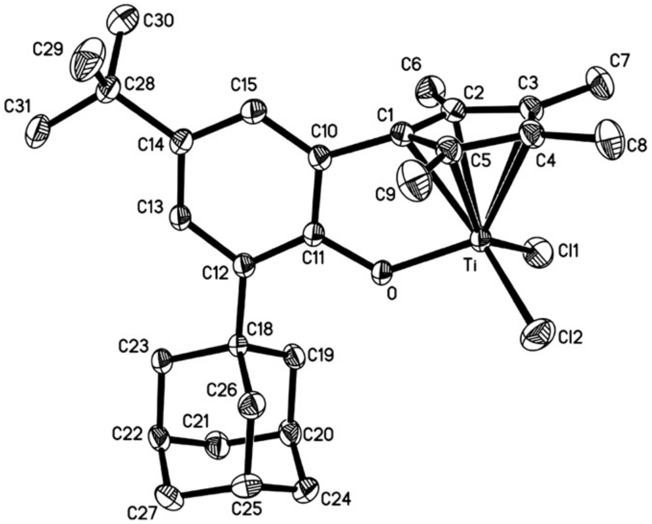


Fig. 2. Structure of complex **9** (thermal ellipsoids are drawn at the 30% probability level).

obviously shorter than those in the known complexes **II** (2.335–2.348 Å) [17], and the Ti–O bond lengths of 1.822(2) Å in **8** and 1.823(2) Å in **9** are also shorter than those in the known complexes **II** (1.832–1.837 Å) [17], which is indicative of good stability of complexes **8** and **9** in comparison with their analogues.

2.3. Copolymerization of ethylene with 1-hexene

Copolymerization of ethylene with 1-hexene using complexes **8**–**10** as catalysts, activated with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$, was explored. For comparison purpose, the catalytic property of a known complex [η^5: η^1-2-C_5Me_4-4,6-$^tBu_2C_6H_2O$]$TiCl_2$ (**11**) was also examined. The copolymerization results are summarized in Table 2. The catalytic activity of these catalysts for the ethylene/1-hexene copolymerization under similar conditions changes in the order of **9** > **8** > **11** > **10**. The catalytic activity of the **10**/TIBA/B catalyst system is obviously lower than other catalyst systems under similar conditions, which should be attributed to the weaker electron-donating ability of the Ph_2Cp ring in **10** comparing to the Me_4Cp ring in other complexes. It is well known for metallocene catalysts that electron-donating groups on the Cp ring would increase the catalytic activity of the catalyst [39]. Except for the electronic effect discussed above, steric effect of the ligands in these complexes on their catalytic activity can be obviously observed by comparing the catalytic activity of **8**, **9** and **11**. Adequately bulky ligand would weaken the interaction between the cationic catalyst and the anionic cocatalyst [16,35], therefore could favor the coordination of the olefins and increase the catalytic activity of the catalyst. Similar results have previously been observed for ethylene/1-hexene copolymerization reaction with other half-metallocene titanium(IV) catalyst systems [19,40,41]. With **9**/TIBA/B catalyst system, copolymerization experiments with different 1-hexene feed concentrations were carried out and obvious comonomer effect was observed. In addition, copolymerization reactions at different temperatures were also examined and the reaction at 70 °C shows the highest catalytic activity. The comonomer content of the obtained poly(ethylene-*co*-1-hexene)s was calculated based on ^{13}C NMR analysis [42], and the molecular weight of the poly(ethylene-*co*-1-hexene)s was measured by GPC. It can be seen from the comonomer content data that the Ph_2Cp based complex **10** shows slightly higher comonomer incorporation ability than the Me_4Cp based complexes **8**, **9** and **11** under similar conditions. GPC analysis reveals that the poly(ethylene-*co*-1-hexene)s produced by the adamantyl-substituted catalysts **8** and **9** possess relatively high molecular weight in comparison to the ones formed from the *tert*-butyl substituted catalyst **11**. The molecular weight distribution is basically unimodal and narrow, being characteristic for metallocene polyolefins.

Table 1
Selected bond lengths and angles for complexes **8** and **9**.

*Complex **8***			
Ti(1)–C(1)	2.305(3)	Ti(1)–C(4)	2.380(3)
Ti(1)–C(2)	2.309(3)	Ti(1)–C(5)	2.371(1)
Ti(1)–C(3)	2.357(3)	Ti(1)–Cl(1)	2.245(1)
Ti(1)–O(1)	1.822(2)	Ti(1)–Cl(2)	2.259(1)
Cl(1)–Ti(1)–O(1)	103.95(6)	Cl(2)–Ti(1)–O(1)	104.59(7)
Cl(1)–Ti(1)–Cl(2)	104.37(4)	Ti(1)–O(1)–C(11)	125.6
O(1)–C(11)	1.383(3)	C(1)–Ti(1)–O(1)	75.42
Ti–C(Cp) (av)	2.011	Cp(cent)–Ti–O	106.5
C(6)–C(1)–Cp(cent)	11.9		
*Complex **9***			
Ti(1)–C(1)	2.298(2)	Ti(1)–C(4)	2.369(2)
Ti(1)–C(2)	2.331(2)	Ti(1)–C(5)	2.323(2)
Ti(1)–C(3)	2.384(2)	Ti(1)–Cl(1)	2.268(1)
Ti(1)–O(1)	1.823(2)	Ti(1)–Cl(2)	2.276(1)
Cl(1)–Ti(1)–O(1)	106.31(7)	Cl(2)–Ti(1)–O(1)	104.12(6)
Cl(1)–Ti(1)–Cl(2)	105.13(4)	Ti(1)–O(1)–C(11)	129.17(13)
O(1)–C(11)	1.367(3)	C(1)–Ti(1)–O(1)	75.17(8)
Ti–C(Cp) (av)	2.007	Cp(cent)–Ti–O	106.7
C(10)–C(1)–Cp(cent)	11.0		

Table 2
Results of ethylene/1-hexene copolymerization with **8**–**11**/Al^iBu_3/$Ph_3CB(C_6F_5)_4$ systems.[a]

Run	Cat	Temp[b] (°C)	1-Hexene[c] (mol/L)	Activity[d] ($\times10^3$)	Incorp[e] (mol%)	M_w[f] ($\times10^3$)	PDI[f]
1	**8**	70	0.3	13.3	7.8	17	2.3
2	**9**	70	0.2	15.1	5.1	18	2.4
3	**9**	70	0.3	16.6	7.6	17	2.3
4	**9**	70	0.4	18.2	10.3	15	2.5
5	**9**	70	0.5	16.8	12.6	13	2.4
6	**9**	50	0.3	11.7	7.3	20	2.4
7	**9**	90	0.3	12.4	7.8	13	2.5
8	**10**	70	0.3	9.5	8.5	9	2.3
9	**11**	70	0.3	12.8	7.7	14	2.6
10	**11**	70	0.5	11.9	12.4	10	2.4

[a] Reaction conditions: ethylene pressure, 5 atm; catalyst, 1 μmol; toluene + 1-hexene total, 80 mL; molar ratio of Al/Ti, 120; molar ratio of B/Ti, 1.5; polymerization time, 10 min.
[b] Polymerization temperature.
[c] Concentration of 1-hexene in feed.
[d] Activity in kg polymer/(mol Ti h).
[e] Determined by ^{13}C NMR.
[f] Determined by GPC, M_w in g/mol.

2.4. ENB polymerization

ENB polymerization reactions catalyzed by the **8**–**10**/TIBA/B catalyst systems were studied in detail and the results are summarized in Table 3. For comparison purpose, polymerization reaction with a known nonbridged (2,6-diisopropyphenoxy)(pentamethylcyclopentadienyl)titanium dichloride complex [C_5Me_5][2,6-$^iPr_2C_6H_2O$]$TiCl_2$ (**12**) [43,44] as catalyst was also examined. The effects of the polymerization temperature and initial ENB concentration on the polymerization reaction were examined with **9**/TIBA/B catalyst system. The catalytic activity, together with the polymer yield and ENB conversion, increases with the elevation in polymerization temperature and reaches their maximum values at about 70 °C. The intrinsic viscosity of the obtained poly(5-ethylidene-2-norbornene) (PENB) decreases with the increase in polymerization temperature, indicating that the molecular weight of the PENB decreases with the elevation in polymerization temperature. The catalytic activity increases with the increase in

Table 3
Results of ENB homopolymerization with **8**–**12**/Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ systems.[a]

Run	Cat.	Temp[b] (°C)	ENB[c] (mol/L)	Yield (g)	Activity[d] ($\times 10^3$)	Conversion (%)	η^e (dL/g)
1	**8**	70	1.0	0.47	78	7.8	0.30
2	**9**	30	1.0	0.49	82	8.1	0.35
3	**9**	50	1.0	0.58	97	9.6	0.33
4	**9**	70	1.0	0.73	121	12.1	0.31
5	**9**	90	1.0	0.67	112	11.1	0.28
6	**9**	70	2.0	1.41	235	11.7	0.45
7	**9**	70	3.0	1.85	308	10.2	0.62
8	**10**	70	1.0	0.39	65	6.5	0.28
9[f]	**11**	70	1.0	0.70	116	11.6	0.27
10	**12**	70	1.0	0.29	48	4.8	0.42

[a] Reaction conditions: catalyst, 2 μmol; molar ratio of Al/Ti, 150; molar ratio of B/Ti, 1.5; toluene + ENB total, 50 mL; polymerization time, 3 h.
[b] Polymerization temperature.
[c] Initial ENB concentration.
[d] Activity in kg polymer/(mol Ti h).
[e] Intrinsic viscosity measured at 135 °C in decahydronaphthalene.
[f] Cited from reference [30].

initial ENB concentration. In addition, the increase in the initial ENB concentration results in an increase in the yield and intrinsic viscosity of the PENB. These results are similar to those observed in the ENB polymerization with **11**/TIBA/B catalyst system [30]. As observed for the ethylene/1-hexene copolymerization, the catalytic activity of the **10**/TIBA/B catalyst system is obviously lower than that of **8** and **9**/TIBA/B catalyst systems under similar conditions. In comparison with the results reported in literature for the constrained geometry (^{t}BuNSiMe$_2$Flu)TiMe$_2$/MAO catalyst system [45], the catalytic activity of the **8**–**10**/TIBA/B catalyst systems for the ENB polymerization is relatively high even at lower polymerization temperature.

^{1}H NMR spectra of several typical PENB samples from different reactions are shown in Fig. 3. In these ^{1}H NMR spectra, obvious differences can be seen in the region of 5.5–6.2 ppm. According to literatures [30,45], the resonances between 6.0 and 6.2 ppm are for the protons of the endocyclic double bond and the resonances between 4.9 and 5.8 ppm are for the double bond protons of the ethylidene group. The ^{1}H NMR spectra of these PENB samples show that ENB is polymerized regioselectively by the **8**–**10**/TIBA/B catalyst systems through the endocyclic double bond with the ethylidene group unreacted [45–47]. The signals of the ethylidene double bond protons can be observed over the region of 4.9–5.8 ppm for the sample produced by catalyst **11** as shown in Fig. 3(c), while the resonances between 5.5 and 5.8 ppm can hardly be observed in Fig. 3(a) and (b) for the samples made with catalyst **9**. The sample obtained with catalyst **12** shows further difference in the proton resonances in this region with stronger signals between 5.5 and 5.8 ppm and narrow signals between 5.0 and 5.2 ppm. These results indicate the difference in microstructure of the PENB samples obtained from different catalyst systems. Even only the major one of the two ENB isomers is considered, there should be three types of triads (as shown in Fig. 4) and ten types of pentads in the PENB polymer chain. It has been known that the C_s-symmetry constrained geometry (^{t}BuNSiMe$_2$Flu)TiMe$_2$/MAO catalyst system catalyzes the ethylene/norbornene copolymerization to produce *racemo*-NN sequence enriched copolymer (*racemo*-NN sequence/*meso*-NN sequence = 11) [45]. On the basis of the above ^{1}H NMR results, it should be reasonable to suppose that the similar C_s-symmetry catalyst **9** may produce *racemo*-ENB–ENB sequence enriched PENB with more *RR* triads (4.9–5.4 ppm) in the polymer chain, while the less bulky catalyst **11**, and especially the flexible nonbridged catalyst **12** may produce PENB with more *meso*-ENB–ENB sequence and thus more *RM* and *MM* triads (5.5–5.8 ppm) in the polymer chain. ^{13}C NMR spectra of the PENB samples give little information on the microstructure of the polymer chain.

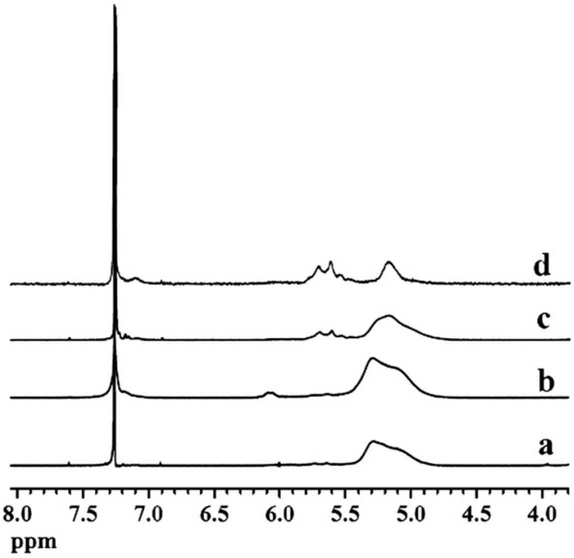


Fig. 3. ^{1}H NMR spectra of typical PENB samples from (a) run 2, (b) run 4, (c) run 9 and (d) run 10 in Table 3 (recorded in CDCl$_3$ at room temperature).

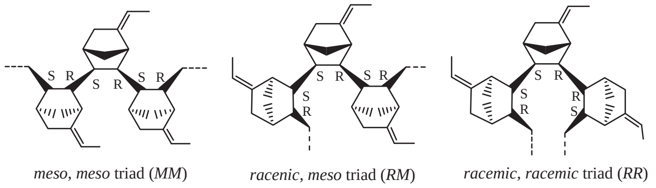
2.5. Copolymerization of ethylene with ENB

The copolymerization of ethylene with ENB catalyzed by the **8**–**10**/TIBA/B catalyst systems under different conditions was investigated. The results, together with those from **11**/TIBA/B catalyst system [30], are summarized in Table 4. As seen above for the ethylene/1-hexene copolymerization and the ENB polymerization, the catalytic activity of **8** and **9**/TIBA/B catalyst systems is higher than that of **10**/TIBA/B catalyst system under the same conditions. The influence of Al/Ti molar ratio on the catalytic activity was examined in the range of 60–150. Maximum catalytic activity was obtained at the Al/Ti molar ratio about 120. The influence of the initial ENB concentration on the E/ENB copolymerization was also examined. For all of these catalyst systems, "comonomer effect" on the catalytic activity was observed with the catalytic activity increasing first and decreasing then after reaching a maximum value as the initial ENB concentration increases from 0.8 to 1.4 mol/L. The content of ENB in the poly(E-*co*-ENB) was calculated based on the ^{1}H NMR spectra according to the following equation [30,45]:

$$\mathrm{ENB\ (mol\%)} = \frac{A}{A + 1/4(B - 11A)}$$

where A is the integral of ethylidene hydrogen signals in the range from 4.8 to 5.3 ppm and B is the integral over all other hydrogen signals from 0.5 to 3.0 ppm. It can be seen from the results in Table 4 that the content of ENB in the poly(E-*co*-ENB)s produced with **8**–**10**/TIBA/B catalyst systems is higher than that in the polymer made with **11**/TIBA/B catalyst system under the same conditions.

The GPC analysis reveals that the obtained poly(E-*co*-ENB) samples possess moderate molecular weights with narrow molecular



meso, meso triad (*MM*) *racenic, meso* triad (*RM*) *racemic, racemic* triad (*RR*)

Fig. 4. Possible microstructures of the PENB triads.

Table 4
Results of E/ENB copolymerization with **8**–**11**/Al^iBu_3/$Ph_3CB(C_6F_5)_4$ systems.[a]

Run	Cat.	Al/Ti[b]	ENB[c] (mol/L)	Yield (g)	Activity[d] ($\times10^3$)	ENB[e] content	M_w[f] ($\times10^3$)	PDI[f]	T_g[g]
1	**9**	60	1.0	0.094	188	n.d.[h]	91	2.4	177.8
2	**9**	90	1.0	0.34	680	n.d.	86	2.3	176.3
3	**9**	120	1.0	0.81	1620	64.6	79	2.2	170.3
4	**9**	150	1.0	0.66	1320	n.d.	73	2.2	173.4
5	**9**	120	0.4	0.41	820	33.1	175	2.3	99.5
6	**9**	120	0.6	0.54	1080	45.2	139	2.3	131.3
7	**9**	120	0.8	0.67	1340	55.8	108	2.2	150.6
8	**9**	120	1.2	0.75	1500	72.9	53	2.3	179.8
9	**9**	120	1.4	0.64	1280	78.6	32	2.2	203.9
10	**8**	120	0.4	0.35	700	32.6	184	2.4	97.4
11	**8**	120	0.6	0.49	980	44.8	141	2.3	130.8
12	**8**	120	0.8	0.62	1240	56.4	106	2.3	152.8
13	**8**	120	1.0	0.74	1480	65.3	77	2.2	171.9
14	**8**	120	1.2	0.71	1420	72.2	52	2.2	180.6
15	**8**	120	1.4	0.62	1220	77.9	31	2.2	199.8
16	**10**	120	0.4	0.29	580	30.7	169	2.5	93.9
17	**10**	120	0.6	0.38	760	41.3	138	2.3	121.6
18	**10**	120	0.8	0.45	900	49.6	115	2.3	141.5
19	**10**	120	1.0	0.51	1020	56.5	102	2.2	151.3
20	**10**	120	1.2	0.47	940	62.4	72	2.2	165.1
21	**10**	120	1.4	0.43	860	67.9	48	2.2	173.7
22	**11**[i]	120	0.8	0.53	1060	41.3	135	2.0	134.6
23	**11**[i]	120	1.4	0.66	1320	50.5	105	2.1	171.9

[a] Reaction conditions: ethylene pressure 1 atm; catalyst, 1 μmol; toluene + ENB total 50 mL, molar ratio of B/Ti 1.5, polymerization time 0.5 h, polymerization temperature, 70 °C.
[b] Molar ratio of Al/Ti.
[c] Initial ENB concentration.
[d] Activity in kg polymer/(mol Ti h).
[e] Determined by ^1H NMR spectroscopy (mol%).
[f] Determined by GPC, M_w in g/mol.
[g] Determined by DSC.
[h] n.d. = not determined.
[i] Cited from reference [30].

weight distribution, suggesting that the polymerization reaction takes place at a single site catalyst [48]. The T_g values of the poly(E-*co*-ENB) samples determined by DSC increase with the increase in the comonomer content, which is similar to the reported results for poly(ethylene-*co*-norbornene)s [29,49] and poly(ethylene-*co*-ENB)s [30,43,44,50–52].

2.6. Conclusions

A number of new constrained geometry titanium complexes, [η^5: η^1-2-C_5Me_4-4-R-6-Ad-C_6H_2O]$TiCl_2$ (**8**–**10**), have been synthesized. These new complexes were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses, and the molecular structures of **8** and **9** were determined by single-crystal X-ray crystallography. Upon activation with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$, these complexes exhibit good catalytic activity for the ethylene/1-haxene and ethylene/ENB copolymerization reactions as well as the ENB polymerization reaction, with the catalytic activity changes in the order of **9** > **8** > **10** under similar conditions. The introduction of the bulky adamantyl substituent to the *ortho* position of the phenoxy group in the ligands of these complexes apparently influences the molecular weight and microstructure of the resultant polymers, as well as the comonomer incorporation ability in the copolymerization of ethylene with ENB.

3. Experimental section

3.1. General comments

Manipulations with organometallic reagents were carried out under a nitrogen atmosphere (ultrahigh purity) using standard Schlenk or glove box techniques. Toluene, diethyl ether, *n*-hexane, and *n*-octane were dried and distilled under nitrogen in the presence of sodium and benzophenone. CH_2Cl_2, 1-hexene and ENB were dried over calcium hydride and distilled or filtered before use. Polymerization grade ethylene was further purified by passage through columns of 5 A molecular sieves and MnO. ^nBuLi, Al^iBu_3 and 5-ethylidene-2-norbornene were purchased from Aldrich or Acros. 3,4-Diphenyl-2-cyclopentenone [53] and $Ph_3CB(C_6F_5)_4$ [54–56] were synthesized according to literature procedures. Other chemical reagents are all commercial available and were used as received. The elemental analyses were performed on a Perkin-Elmer 2400 analyzer. ^1H and ^{13}C NMR spectra were measured on either a Bruker Avance-500 or a Varian Mercury-300 NMR spectrometer. ^{13}C NMR spectra of the copolymers were recorded on a Varian Unity-400 NMR spectrometer at 125 °C with *o*-$C_6D_4Cl_2$ as the solvent. The intrinsic viscosity of the PENB samples was measured in decahydronaphthalene at 135 °C with an Ubbelohde viscometer. Molecular weight and Molecular weight distribution of the copolymer samples were measured on a PL-GPC 220 at 140 °C with 1,2,4-trichlobenzene as the solvent. The melting transition temperature of the polymers was measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C/min and the data from the second heating scan were used.

3.2. Synthesis of 2-adamantyl-4-methylphenol (**1**)

In a dried flask, *p*-cresol (2.142 g, 19.8 mmol), 1-bromoadamantane (4.260 g, 19.8 mmol), $AlCl_3$ (1.60 g, 12.0 mmol), and *n*-octane (60 mL) were mixed under nitrogen at room temperature. The mixture was heated to boiling and stirred for 3 days. After the reaction mixture was cooled to room temperature, the reaction was quenched with 6 N HCl solution (60 mL). After the mixture was vigorously shaken, the organic phase was separated and dried over anhydrous $MgSO_4$. Removal of the solvent on a rotary evaporator left a residue, which was purified by column chromatography on silica gel eluting with hexanes/ethyl acetate (v/v, 30:1) to give a white solid (2.288 g, 9.44 mmol, 47.6%). Anal. Calcd for $C_{17}H_{22}O$ (242.36): C, 84.25; H, 9.15. Found: C, 84.19; H, 9.10. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 6.992 (s, 1H, Ar*H*), 6.841 (d, 1H, Ar*H*), 6.530 (d, 1H, Ar*H*), 4.560 (br, 1H, O*H*), 2.253 (s, 3H, C*H*$_3$), 2.102 (br, 6H, Ad*H*), 2.059 (br, 3H, Ad*H*), 1.760 (br, 6H, Ad*H*).

3.3. Synthesis of 2-adamantyl-4-tert-butylphenol (**2**)

Compound **2** was prepared in the same way as described above for **1** with 4-*tert*-butylphenol (2.974 g, 19.8 mmol) as starting material. Pure product (3.072 g, 10.8 mmol, 54.5%) was obtained as white crystalline material. Anal. Calcd for $C_{20}H_{28}O$ (284.44): C, 84.45; H, 9.92. Found: C, 84.41; H, 9.87. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.230 (s, 1H, Ar*H*), 7.069 (d, 1H, Ar*H*), 6.592 (d, 1H, Ar*H*), 4.590 (br, 1H, O*H*), 2.087 (br, 6H, Ad*H*), 2.053 (br, 3H, Ad*H*), 1.786 (br, 6H, Ad*H*), 1.301 (s, 9H, ^tBu).

3.4. Synthesis of 2-bromo-4-methyl-6-adamantylphenol (**3**)

A solution of Br_2 (0.65 mL, 13 mmol) in chloroform (10 mL) was added dropwise to a solution of **1** (2.957 g, 12.2 mmol) in 20 mL of chloroform at 0 °C during a period of 3 h. The mixture was stirred for another 3 h at this temperature, and then a solution of $NaHSO_3$ (0.1 g) in 15 mL H_2O was added. The mixture was stirred for 30 min and the organic layer was separated and dried over $MgSO_4$. Removal of the solvent on a rotary evaporator gave the crude product, which was washed with pet ether to give the pure product (3.566 g, 11.1 mmol, 91.0%) as white crystalline material. Anal. Calcd for $C_{17}H_{21}BrO$ (321.25): C, 63.56; H, 6.59. Found: C, 63.52; H, 6.53. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.128 (s, 1H, Ar*H*), 6.929 (s, 1H, Ar*H*), 5.605 (s, 1H, O*H*), 2.230 (s, 3H, C*H*$_3$), 2.077 (br, 6H, Ad*H*), 2.054 (br, 3H, Ad*H*), 1.749 (br, 6H, Ad*H*).

3.5. Synthesis of 2-bromo-4-tert-butyl-6-adamantylphenol (4)

Compound **4** was prepared in the same way as described above for **3** with **2** (2.825 g, 9.93 mmol) as starting material. Pure product (3.324 g, 9.15 mmol, 92.1%) was obtained as white crystalline material. Anal. Calcd for $C_{20}H_{27}BrO$ (363.33): C, 66.12; H, 7.49. Found: C, 66.06; H, 7.44. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 7.317 (s, 1H, Ar*H*), 7.188 (s, 1H, Ar*H*), 5.650 (s, 1H, O*H*), 2.135 (br, 6H, Ad*H*), 2.080 (br, 3H, Ad*H*), 1.778 (br, 6H, Ad*H*), 1.283 (s, 9H, ^{t}Bu).

3.6. Synthesis of 2-(tetramethylcyclopentadienyl)-4-methyl-6-adamantylphenol (5)

A solution of **3** (3.100 g, 9.65 mmol) in Et$_2$O (20 mL) was slowly added to a solution of ^{n}BuLi (21 mmol) in Et$_2$O (20 mL) at −15 °C. The mixture was slowly warmed to room temperature and stirred for 5 h. To the solution was slowly added 2,3,4,5-tetramethylcyclopentenone (1.45 mL, 9.65 mmol) in Et$_2$O (10 mL) at 0 °C. The resulting solution was then allowed to warm to room temperature and stirred overnight. The reaction mixture was hydrolyzed with 20 mL of concentrated HCl, and the organic layer was separated, washed three times with water (50 mL) and dried over MgSO$_4$. Removal of the solvent on a rotary evaporator left a brownish oil. Pure product (1.603 g, 4.42 mmol, 45.8%) was obtained by column chromatography over silica (hexanes/CH$_2$Cl$_2$, 9:1) as a yellow crystalline material. Anal. Calcd for $C_{26}H_{34}O$ (362.55): C, 86.13; H, 9.45. Found: C, 86.09; H, 9.41. ^{1}H NMR (CDCl3, 300 MHz, 298 K): δ 6.802 (s, 1H, Ar*H*), 6.778 (s, 1H, Ar*H*), 3.054 (s, 1H, O*H*), 2.576 (q, 1H, Cp*H*), 2.239 (s, 3H, C*H*$_3$), 2.019 (br, 9H, Ad*H*), 1.734 (br, 6H, Ad*H*), 1.623 (s, 3H, C$_5$*Me*$_4$), 1.537 (s, 3H, C$_5$*Me*$_4$), 1.519 (s, 3H, C$_5$*Me*$_4$), 1.166 (d, 3H, C$_5$*Me*$_4$) ppm.

3.7. Synthesis of 2-(tetramethylcyclopentadienyl)-4-tert-butyl-6-adamantylphenol (6)

Compound **6** was prepared in the same way as described above for **5** with compound **4** (1.360 g, 3.74 mmol) as starting material. Pure product (0.725 g, 1.79 mmol, 47.9%) was obtained as a white crystal. Anal. Calcd for $C_{29}H_{40}O$ (404.63): C, 86.08; H, 9.96. Found: C, 85.93; H, 9.92. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 7.037 (s, 1H, Ar*H*), 7.019 (s, 1H, Ar*H*), 3.102 (s, 1H, O*H*), 2.373 (q, 1H, Cp*H*), 2.057 (br, 9H, Ad*H*), 1.760 (br, 6H, Ad*H*), 1.592 (s, 3H, C$_5$*Me*$_4$), 1.585 (s, 3H, C$_5$*Me*$_4$), 1.561 (s, 3H, C$_5$*Me*$_4$), 1.295 (s, 9H, ^{t}Bu), 1.221 (d, 3H, C$_5$*Me*$_4$).

3.8. Synthesis of 2-(diphenylcyclopentadienyl)-4-tert-butyl-6-adamantylphenol (7)

A solution of **4** (2.402 g, 6.61 mmol) in Et$_2$O (20 mL) was slowly added to a solution of ^{n}BuLi (15 mmol) in Et$_2$O (20 mL) at −15 °C. The mixture was slowly warmed to room temperature and stirred for 5 h. After the solvent was removed, the residue was suspended in toluene (40 mL). To the suspension was dropwise added a solution of 3,4-diphenyl-2-cyclopentenone (1.542 g, 6.61 mmol) in toluene (20 mL) at −15 °C over an hour. The reaction mixture was stirred at room temperature overnight and 65 °C for further 4 h, then quenched with 20 mL of saturated NH$_4$Cl (aq). The organic layer was separated, washed three times with water (40 mL) and dried over MgSO$_4$. Removal of the solvent on a rotary evaporator left a brownish residue. Pure product (1.178 g, 2.35 mmol, 35.6%) was obtained by column chromatography over silica (hexanes/CH$_2$Cl$_2$, 1:2) as yellow needles. Anal. Calcd for $C_{37}H_{40}O$ (500.71): C, 88.75; H, 8.05. Found: C, 88.66; H, 7.98. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 7.33–7.45 (m, 4H, Ar*H*), 7.17–7.27 (m, 8H, Ar*H*), 5.575 (s, 1H, O*H*), 3.951 (s, 2H, Cp*H*), 2.322 (br, 6H, Ad*H*), 2.154 (br, 3H, Ad*H*), 1.863 (s, 6H, Ad*H*), 1.225 (s, 9H, ^{t}Bu).

3.9. Synthesis of [η^5: η^1-2-C$_5$Me$_4$-4-Me-6-Ad-C$_6$H$_2$O]TiCl$_2$ (8)

A solution of **5** (0.550 g, 1.52 mmol) in toluene (15 mL) was slowly added to a solution of TiCl$_4$ (1.52 mmol) in toluene (30 mL) at room temperature. The mixture was stirred at 60 °C overnight. The precipitate was filtered off, and the solvent was removed to leave the crude product. Pure product (0.614 g, 1.28 mmol, 84.2%) was obtained as red crystals by recrystallization from CH$_2$Cl$_2$/hexane (v/v 1:3). Anal. Calcd for $C_{26}H_{32}Cl_2OTi$ (479.30): C, 65.15; H, 6.73. Found: C, 64.92; H, 6.87. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 7.064 (s, 1H, Ar*H*), 6.914 (s, 1H, Ar*H*), 2.414 (s, 6H, C$_5$*Me*$_4$), 2.396(s, 3H, C*H*$_3$), 2.050 (br, 6H, Ad*H*), 2.031 (s, 6H, C$_5$*Me*$_4$), 2.028 (br, 3H, Ad*H*), 1.753 (br, 6H, Ad*H*). ^{13}C NMR (CDCl$_3$, 75 MHz, 298 K): δ 172.65, 145.10, 142.96, 136.56, 133.43, 129.99, 129.81, 126.80, 41.17, 37.35, 37.15, 29.29, 21.26, 13.27, 12.68.

3.10. Synthesis of [η^5: η^1-2-C$_5$Me$_4$-4-^{t}Bu-6-Ad-C$_6$H$_2$O]TiCl$_2$ (9)

Complex **9** was synthesized in the same way as described above for complex **8** with compound **6** (0.611 g, 1.51 mmol) and TiCl$_4$ (1.51 mmol) as starting material. Pure product (0.692 g, 1.35 mmol, 89.4%) was obtained as red crystals. Anal. Calcd for $C_{29}H_{38}Cl_2OTi$ (521.38): C, 66.81; H, 7.35. Found: C, 66.72; H, 7.43. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 7.579 (d, 1H, Ar*H*), 7.177 (d, 1H, Ar*H*), 2.342 (br, 6H, Ad*H*), 2.123 (s, 6H, C$_5$*Me*$_4$), 2.065 (br, 3H, Ad*H*), 1.934 (s, 6H, C$_5$*Me*$_4$), 1.833, 1.732 (dd, br, 6H, Ad*H*), 1.439 (s, 9H, ^{t}Bu). ^{13}C NMR (CDCl$_3$, 75 MHz, 298 K): δ 172.43, 146.99, 145.24, 143.33, 136.04, 129.98, 129.58, 123.69, 123.11, 41.26, 37.70, 37.14, 34.91, 31.88, 29.30, 13.35, 12.73.

3.11. Synthesis of [η^5: η^1-2-Ph$_2$C$_5$H$_2$-4-^{t}Bu-6-Ad-C$_6$H$_2$O]TiCl$_2$ (10)

A solution of ^{n}BuLi (4.0 mmol) in Et$_2$O (10 ml) was slowly added to a solution of **7** (1.001 g, 2.00 mmol) in Et$_2$O (20 mL) at −20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. After the solvent was removed, the residue was washed with hexanes and redissolved in toluene (25 mL). To the solution was dropwise added a solution of TiCl$_4$ (2.0 mmol) in toluene (15 mL) at −40 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The precipitate was filtered off, and the solvent was removed to leave a red solid. Recrystallization from CH$_2$Cl$_2$/hexane (1:3) gave pure **10** as red crystals (0.561 g, 0.908 mmol, 45.4%), Anal. Calcd for $C_{37}H_{38}Cl_2OTi$ (617.47): C, 71.97; H, 6.20. Found: C, 71.74; H, 6.37. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 7.58–7.60 (m, 4H, Ph*H*), 7.569 (d, 1H, Ar*H*), 7.265 (d, 1H, Ar*H*), 7.07–7.11 (m, 6H, Ph*H*), 6.398 (s 2H, Cp*H*), 2.415 (br, 6H, Ad*H*), 2.123 (br, 3H, Ad*H*), 1.883, 1.760 (dd, 6H Ad*H*), 1.515 (s, 9H, ^{t}Bu). ^{13}C NMR (C$_6$D$_6$, 75 MHz, 298 K): δ 172.38, 147.33, 145.64, 135.50, 133.11, 133.02, 131.94, 131.13, 130.02, 129.16, 128.41, 123.46, 123.29, 41.49, 37.73, 37.11, 35.02, 31.89, 29.33.

3.12. X-ray structure determination

X-ray data were collected at 293 K on a Siemens P4 four-circle diffractometer for **8** and a Bruker SMART-CCD diffractometer for **9** (graphite-monochromated Mo KR radiation: $l = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 5. The structures were solved by direct methods [57] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All

Table 5
Crystallographic data and structural refinement details for complexes **8** and **9**.

	8	**9**
mol formula	$C_{26}H_{32}Cl_2OTi$	$C_{29}H_{38}Cl_2OTi$
Mol wt	479.32	521.39
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a/Å	7.3163(11)	10.095(2)
b/Å	19.168(3)	10.579(2)
c/Å	17.210(3)	13.532(3)
α/deg	90	93.73(3)
β/deg	90.526(2)	107.57(3)
γ/deg	90	95.03(3)
V/Å^3	2413.4(6)	1366.0(5)
Z	4	2
D_c/g cm^{-3}	1.319	1.268
F(000)	1008	552
Abs coeff/mm^{-1}	0.591	0.528
Scan type	ω–2θ	ω–2θ
Collect range, deg	$1.59 \le 2\theta \le 26.07$	$3.01 \le 2\theta \le 27.48$
No. of reflns	13,368	13,562
No. of indep reflns	4749	6211
R_{int}	0.0555	0.0244
No. of data/restraints/params	4749/0/277	6211/0/305
R ($I > 2$sigma(I))	0.0502	0.0434
R_w ($I > 2$sigma(I))	0.1138	0.1147
Goodness of fit	0.950	1.052
Largest diff peak	0.504	0.585
And hole/e Å^{-3}	−0.318	−0.410

calculations were performed using the SHELXTL [58] crystallographic software packages.

3.13. *Ethylene/1-hexene copolymerization*

The ethylene/1-hexene copolymerization experiments were carried out as follows: A dry 250 mL steel autoclave with a magnetic stirrer was charged with 70 mL of 1-hexene solution in toluene, thermostated at desired temperature and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of catalyst and Al^{i}Bu$_3$ in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately and the pressure was kept by continuously feeding of ethylene. After the reaction mixture was stirred at the desired temperature for 10 min, the polymerization was quenched by injecting acidified ethanol containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum.

3.14. *General procedure of ENB polymerization and E/ENB copolymerization*

ENB polymerization experiments were performed as follows: a dry 100 mL flask with a magnetic stirrer was charged with a solution of appropriate amount of ENB and Al^{i}Bu$_3$ (2/3 of total amount) in toluene (40 mL) under N_2, thermostated at the desired temperature in an oil bath. The polymerization reaction was started by injection of a mixture of a catalyst and Al^{i}Bu$_3$ (1/3 of total amount) in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. After a certain period of time, the polymerization was terminated by injecting acidified methanol [HCl (3 M)/methanol 1:1]. The polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight.

E/ENB copolymerization experiments were performed in a similar way: a dry 100 mL flask with a magnetic stirrer was charged with a solution of appropriate amount of ENB and AliBu$_3$ (2/3 of total amount) in toluene (40 mL), thermostated at the desired temperature, and saturated with ethylene (1 atm). The polymerization reaction was started by injection of a mixture of a catalyst and Al^{i}Bu$_3$ (1/3 of total amount) in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. After a certain period of time, the polymerization was quenched by injecting acidified methanol. The polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight.

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Appendix A. Supplementary material

CCDC 804461 and 804462 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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