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Facile, Efficient Copolymerization of Ethylene with Bicyclic, Non-Conjugated Dienes by Titanium Complexes Bearing Bis(β-Enaminoketonato) Ligands

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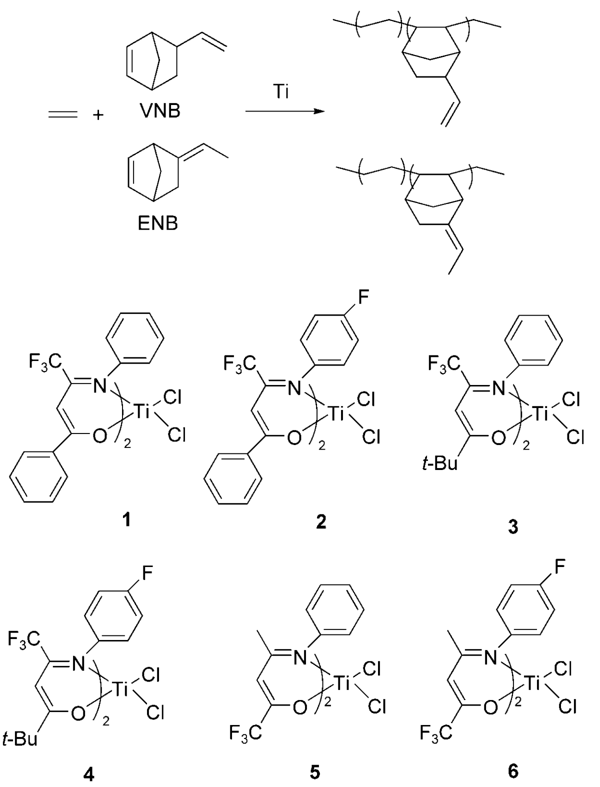
Abstract: Copolymerizations of ethylene with 5-vinyl-2-norbornene or 5-ethylidene-2-norbornene under the action of various titanium complexes bearing bis(β-enaminoketonato) chelate ligands of the type, $[R^1N{=}C(R^2)CH{=}C(R^3)O]_2TiCl_2$ (**1**, $R^1=$ Ph, $R^2=CF_3$, $R^3=$ Ph; **2**, $R^1=C_6H_4F$-*p*, $R^2=CF_3$, $R^3=$ Ph; **3**, $R^1=$ Ph, $R^2=CF_3$, $R^3=t$-Bu; **4**, $R^1=C_6H_4F$-*p*, $R^2=CF_3$, $R^3=t$-Bu; **5**, $R^1=$ Ph, $R^2=CH_3$, $R^3=CF_3$; **6**, $R^1=C_6H_4F$-*p*, $R^2=CH_3$, $R^3=CF_3$), have been shown to occur with the regioselective insertion of the endocyclic double bond of the monomer into the copolymer chain, leaving the exocyclic vinyl double bond as a pendant unsaturation. The ligand modification strongly affects the copolymerization behaviour. High catalytic activities and efficient co-monomer incorporation can be easily obtained by optimizing the catalyst structures and polymerization conditions.

Keywords: copolymerization; ethylene; norbornene derivatives; titanium

The synthesis of polyolefins bearing pendant double bonds has attracted considerable attention in recent years. This is primarily because the pendant double bonds of the poly(olefin)s can be easily converted into functional groups by further chemical transformations, which offers then sites for initiating graft copolymerization.[1] A facile route to obtain such modified poly(olefin)s is the copolymerization of an olefin with an α,ω-diene, which is much less harmful to the catalyst. The use of classical Ziegler–Natta catalysts for ethylene/α,ω-diene copolymerization is limited due to the poor catalytic activity, low diene incorporation, and broad molecular weight distributions.[2] Metallocene catalysts have been widely employed to promote ethylene/diene copolymerizations. However, undesirable cross-linking and/or cyclopolymerization reactions may occur if linear symmetrical dienes, like 1,5-hexadiene and 1,7-octadiene, are used.[3–5] A better access that has been more recently developed is the use of cyclodiolefins, such as vinycyclohexene, 1,3-cyclohexadiene, 2,5-norbornadiene, and dicyclopentadiene, as the co-monomers. These dienes are very attractive because cyclization and cross-linking reactions are not likely to occur in the copolymerization with ethylene due to their unique chemical structure. A number of metallocene and half-metallocene complexes were efficiently tested to produce ethylene/cyclodiolefin copolymers.[6–8] Nevertheless, successful examples concerning the controlled copolymerization by non-Cp transition metal catalysts are limited so far.[9a]

Our interest is to explore ethylene/cycloolefin copolymerizations with group 4 non-metallocene catalysts and, further, to prepare poly(olefin)s bearing an unsaturated carbon-carbon bond in the side chain. The two norbornene derivatives, 5-vinyl-2-norbornene (VNB) and 5-ethylidene-2-norbornene (ENB) with pendant C=C double bond (vinyl and vinylidene), have been selected as the precursor monomers to introduce functional groups. In this paper, we thus report the copolymerization of ethylene with VNB or ENB by the action of titanium complexes bearing two β-enaminoketonato ligands. These titanium complexes activated with modified methylaluminoxane (MMAO) display remarkable catalytic activity and copolymerization ability. As expected, the enchainment of the cyclic monomer occurred selectively through the endocyclic double bond, leaving a reactive pendant unsaturation free (Scheme 1).

Various titanium complexes containing bis(β-enaminoketonato) chelate ligands of the type, $[R^1N{=}C(R^2)CH{=}C(R^3)O]_2TiCl_2$ (**1**, $R^1=$ Ph, $R^2=CF_3$, $R^3=$ Ph; **2**, $R^1=C_6H_4F$-*p*, $R^2=CF_3$, $R^3=$ Ph; **3**, $R^1=$ Ph, $R^2=CF_3$, $R_3=t$-Bu; **4**, $R^1=C_6H_4F$-*p*, $R^2=CF_3$, $R^3=t$-Bu; **5**, $R^1=$ Ph, $R^2=CH_3$, $R^3=CF_3$; **6**, $R^1=C_6H_4F$-*p*, $R^2=CH_3$, $R^3=CF_3$), have been chosen, since they displayed excellent ability to copolymerize ethylene with



Scheme 1.

strained norbornene and cyclopentene, affording high molecular weight copolymers with high co-monomer incorporation.[9b,c]

Copolymerization of ethylene with 5-vinyl-2-norbornene: Ethylene undergoes facile copolymerization with VNB in toluene under different conditions. The typical data for the copolymerizations are summarized in Table 1. Complex **1** showed high catalytic activity and excellent ability to incorporate VNB into polymer chains although the activity decreased with increasing co-monomer content in the feed (entries 1 and 2). The copolymers with high VNB content were completely soluble in toluene at 50 °C, indicating that the cross-linking was negligible. The molecular weight (M_w) of the resultant copolymer was first investigated by high temperature gel permeation chromatography analysis in 1,2,4-trichlorobenzene. However, at high cycloolefin incorporation levels, the GPC data using the RI detector became inaccurate. The signal to noise ratio decreased due to the decreasing difference of refractive index between the polymer solution and the solvent used, as reported in the literature.[7c] Therefore, we measured the M_w by a Waters instrument eluting with THF at 25 °C. The copolymer obtained with **1** possessed relatively high moelcular weights (M_w = 288–376 kg mol^{-1}) with narrow and unimodal molecular weight distributions (MWDs, $M_\mathrm{w}/M_\mathrm{n}$ = 1.38–1.48).

The incorporation and regioselectivity of the unconjugated cyclic diene are estimated by ^{1}H and

Table 1. Copolymerization of ethylene with 5-vinyl-2-norbornene by bis(β-enaminoketonato)titanium/MMAO catalytic systems.[a]

Entry	Catalyst (μmol)	Al/Ti	VNB [mol/L]	Temp. [°C]	Pressure [atm]	Yield [g]	Activity [kg mol^{-1} h^{-1}]	M_w[b] [×10^{-4}]	M_w/M_n[b]	Monom. Incorp. [%][c]
1	**1** (3.0)	1000	0.2	25	1	0.30	600	37.6	1.38	23.6
2	**1** (3.0)	1000	1.0	25	1	0.16	320	34.3	1.35	38.9
3	**1** (3.0)	4000	0.2	25	1	0.35	700	38.6	1.42	21.8
4	**1** (3.0)	4000	1.0	25	1	0.17	340	28.8	1.48	31.3
5	**1** (3.0)	1000	0.2	50	1	0.24	480	27.0	1.49	22.3
6	**1** (3.0)	1000	1.0	50	1	0.11	220	25.4	1.46	38.1
7	**1** (3.0)	1000	0.2	25	4	1.01	2020	–[d]		9.2
8	**1** (3.0)	1000	1.0	25	4	0.81	1620	–[d]		21.2
9	**2** (3.0)	1000	0.2	25	1	0.13	260	29.1	1.41	25.1
10	**2** (3.0)	1000	1.0	25	1	0.10	200	22.3	1.50	33.5
11	**3** (3.0)	1000	0.2	25	1	0.39	780	bimodal		–
12	**3** (3.0)	1000	1.0	25	1	0.15	300	bimodal		–
13	**4** (3.0)	1000	0.2	25	1	0.27	540	bimodal		–
14	**4** (3.0)	1000	1.0	25	1	0.10	200	bimodal		–
15	**5** (3.0)	1000	0.2	25	1	0.51	1020	bimodal		–
16	**5** (3.0)	1000	1.0	25	1	0.20	400	bimodal		–
17	**6** (3.0)	1000	0.2	25	1	0.19	380	bimodal		–
18	**6** (3.0)	1000	1.0	25	1	0.13	260	bimodal		–

[a] *Conditions:* 10 min, V_total = 30 mL.
[b] GPC data in THF *vs.* polystyrene standards.
[c] VNB incorporation (mol%) established from the ^{1}H NMR spectra.
[d] Insoluble in THF.

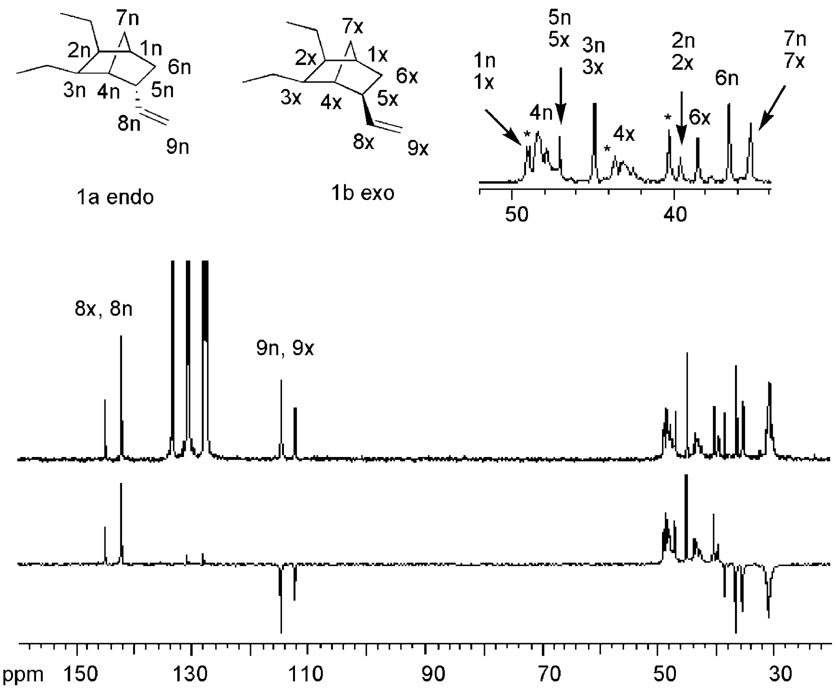


Figure 1. Selected ^{13}C NMR spectra (in *o*-$C_6D_4Cl_2$ at 110 °C) for poly(ethylene-*co*-VNB) prepared by **1**/MMAO catalyst system. (entry 2 in Table 1, with VNB incorporation 38.9%). The resonances marked with asteriks are ascribed to the alternating sequence.

^{13}C NMR. All resonances were identified by the DEPT analysis and the comparison with those of poly-(ethylene-*co*-5-vinyl-2-norbornene)s reported.[7c,d] Increasing VNB concentration significantly enhanced the VNB incorporation, and the copolymers containing as high as 38.9 mol% VNB can be easily achieved under the mild conditions (entry 2 in Table 1). As expected, the enchainment of the cyclic monomer occurred selectively *via* the 2,3-addition of the endocyclic double bond. The ^{1}H NMR spectra of the copolymer showed a typical vinyl pattern between 4.8 and 6.0 ppm (exocyclic olefin) and the absence of an intense triplet around 6.1 ppm (endocyclic olefin). The two main sequences **1a** (*endo*) and **1b** (*exo*) of the poly(ethylene-*co*-VNB) are presented in Figure 1. The ^{13}C NMR spectrum of the copolymer (entry 2 in Table 1) showed the peaks at 144.37 (=CH, *exo*), 141.70 (=CH, *endo*), 113.78 (=CH_2, *endo*), and 111.30 ppm (=CH_2, *exo*), but no peak at 136.9 ppm, which indicates the presence of a vinyl double bond and the absence of the endocyclic double bond (Figure 1). The *endo/exo*-position of the vinyl double bond significantly influenced the chemical shifts of carbon group 6 both in ^{1}H and ^{13}C NMR spectra. For example, the resonance in the ^{13}C NMR spectrum of the copolymer detected at 36.5 and 38.4 ppm can be assigned to 6n and 6x, respectively. However, little effect on the bridge carbon 7 was observed. The resonances arising from 7n and 7x overlapped in the ^{13}C NMR spectra. The copolymer displayed isolated VNB inserted units and E/VNB alternating sequences, as shown in Figure 1. The intensities of these resonances were significantly enhanced with the increase of VNB incorporation. The resonances ascribed to repeated VNB insertion were negligible, and this fact may clearly explain that negligible or no catalytic activity was observed in an attempted homopolymerization of VNB by **1**.

The copolymerization reactions carried out with different Al/Ti ratios by **1** are also listed in Table 1. Under low VNB concentrations, the increase in Al/Ti molar ratio caused no significant changes either in the catalytic activity or the moledular weughts for the resultant poly(ethylene-*co*-VNB)s (entry 1 *vs.* 3). Moreover, VNB incorporation was also independent of the Al/Ti molar ratio. This result suggests that the dominant chain-transfer pathway is not chain-transfer to aluminum alkyls but seems to be β-hydrogen elimination under these conditions. The observed catalytic activity and the molecular weight of the copolymer decreased when the copolymerization was conducted at a higher temperature under the same condition (entry 1 *vs.* 5). Moreover, the molecular weight depended on the reaction pressure, a significant enhancement in molecular weight was seen if the copolymerization was done under 4 atm ethylene pressure (entry 7 in Table 1). This result also supports the above suggestion that the dominant chain-transfer would be the β-hydrogen elimination from propagating metal-alkyl species. In contrast, at high VNB

Table 2. Copolymerization of ethylene with 5-ethylidene-2-norbornene (ENB) by bis(β-enaminoketonato)titanium/MMAO catalytic systems.[a]

Entry	Catalyst (μmol)	Al/Ti	ENB [mol/L]	Temp. [°C]	Time [min]	Yield [g]	Activity [kg mol^{-1}$_{\mathrm{Ti}}$·h]	M_w[b] [×10^{-4}]	M_w/M_n[b]	ENB incorp. [%][c]
1	1 (3.0)	1000	0.2	25	10	0.56	1120	41.6	1.33	25.8
2	1 (3.0)	1000	1.0	25	10	0.53	1060	40.3	1.29	28.3
3	2 (3.0)	1000	0.2	25	10	0.16	320	34.3	1.51	26.5
4	2 (3.0)	1000	1.0	25	10	0.29	580	31.1	1.47	29.3
5	3 (3.0)	1000	0.2	25	10	0.25	500	bimodal		–
6	3 (3.0)	1000	1.0	25	10	0.34	680	bimodal		–
7	4 (3.0)	1000	0.2	25	10	0.24	480	bimodal		–
8	4 (3.0)	1000	1.0	25	10	0.51	1020	bimodal		–
9	5 (0.5)	1000	0.2	25	10	0.53	6360	47.1	1.24	31.0
10	5 (0.5)	1000	1.0	25	10	0.75	9000	54.4	1.20	34.7
11	5 (0.5)	4000	0.2	25	10	0.69	8280	41.1	1.28	29.5
12	5 (0.5)	4000	1.0	25	10	1.14	13700	46.7	1.31	35.7
13	5 (0.5)	1000	0.2	25	3	0.19	7600	47.1	1.18	30.4
14	5 (0.5)	1000	0.2	25	5	0.39	9360	46.7	1.23	31.2
15	5 (0.5)	1000	0.2	50	10	0.18	2160	37.5	1.51	34.2
16	5 (0.5)	1000	1.0	50	10	0.30	3600	44.0	1.29	41.1
17	6 (3.0)	1000	0.2	25	10	0.77	1540	bimodal		–
18	6 (3.0)	1000	1.0	25	10	0.56	1120	bimodal		–

[a] *Conditions:* ethylene 1 atm, $V_{\mathrm{total}} = 30$ mL.

[b] GPC data in THF *vs.* polystyrene standards.

[c] ENB incorporation established from the ^{1}H NMR spectra.

feeds, the tendency to undergo β-hydrogen elimination decreased, and the chain-transfer to aluminum alkyls was observed. The evidence came from the fact that the molecular weights decreased upon increasing the cocatalyst concentration (entry 2 *vs.* 4).

The data in Table 1 indicate that VNB incorporation and the molecular weight of the copolymers were significantly influenced by catalyst structures. Catalyst **2** bearing a *para*-fluorine atom on the *N*-aryl moiety in the ligand showed low catalytic activity, affording polymers with high molecular weight and unimodal molecular weight distributions (MWDs) (entries 9 and 10). Species **3** and **4** have comparable structures with **1** and **2**, but they produced bimodal molecular weight distribution polymers under the same conditions (entries 11–15). Similar phenomena were observed for **5** and **6** (entries 15–18). Since **3–6** did not show multi-site characteristics in the copolymerization with α-olefin and cyclyolefin, there appears no clear reason at this moment why they afforded poly(E-*co*-VNB)s with bimodal MWDs. One possible explanation is that the exocyclic vinyl double bond significantly influenced polymerization behaviours and the conjugated phenyl group in the R^3 position of the ligands is much favoured for stabilizing the active species and getting high molecular weight polymers with unimodal MWDs for copolymerization with VNB.

Copolymerization of ethylene with 5-ethylidene-2-norbornene: Copolymerizations of ethylene with ENB by complexes **1–6** were also investigated under similar conditions. The polymerization results are summarized in Table 2. All the catalytic systems employed were able to copolymerize ethylene with ENB. The resultant copolymers displayed different MWs, MWDs, and co-monomer incorporations under the same conditions. Compared with VNB, ENB causes less important decrease both in productivity and the molecular weight values.

It was revealed that **1** exhibited high catalytic activity with efficient ENB incorporation, and the catalytic activity towards the copolymerization was much higher than that for ethylene/VNB copolymerization (entries 1 and 2). The poly(E-*co*-ENB)s obtained with **1** were also soluble in THF (GPC solvent) at room temperature and gave the unimodal GPC traces with high molecular wieghts and narrow MWDs. Both the catalytic activity and copolymer molecular weight were almost independent of the concentration of ENB in feed. The activity significantly decreased if **2** was employed in place of **1** under the same conditions (entries 3 and 4). Catalysts **3** and **4** showed moderate catalytic activity for copolymerization with ENB, affording bimodal MWD polymers (entries 5–8 in Table 2). Analogue **5** showed a remarkable catalytic activity, and the activity towards the copolymerization was found to be still higher than that for ethylene homopolymerization.[9b] Note that **5** showed the bimodal molecular weight distributions with VNB, but very narrow molecular weight distributions with ENB. We assumed that the difference in structures between

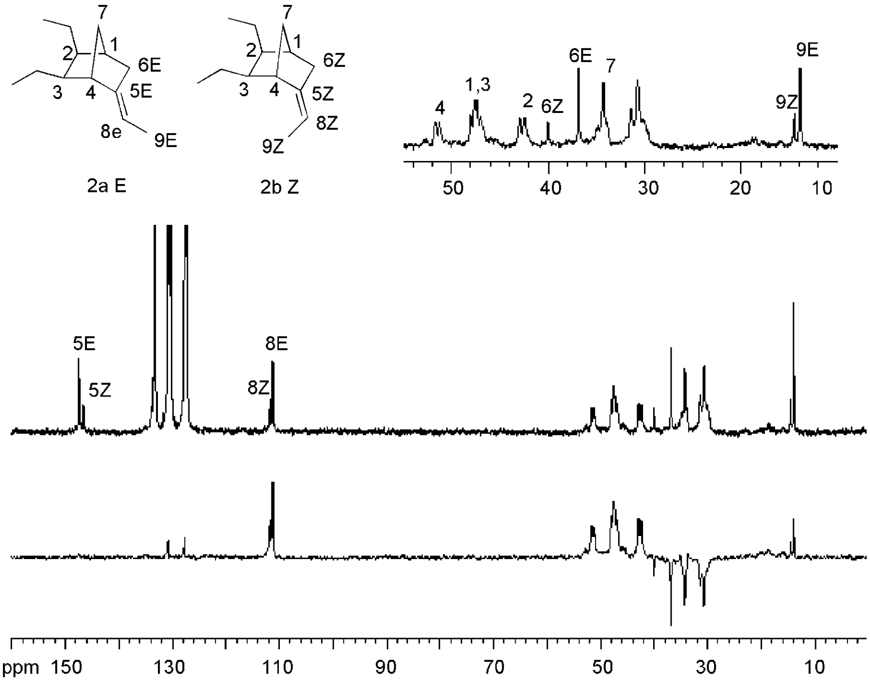


Figure 2. Selected ^{13}C NMR spectra (in *o*-$C_6D_4Cl_2$ at 110 °C) for poly(ethylene-*co*-ENB) prepared by **2**/MMAO catalyst system. (entry 10 in Table 2, with ENB incorporation 34.7%).

VNB and ENB were responsible for this issue. The exocyclic vinyl double bond is rotary for VNB, but it located in the same plane with two carbons in norbornene ring (C4 and C6) for ENB. In addition, both the catalytic activity and the molecular weight of the polymer by **5** increased upon increasing the initial ENB concentration (entries 9 and 10), in complete contrast to the case of ethylene/VNB copolymerization. Therefore, **5** is more suitable catalyst precursor for this copolymerization in terms of high catalytic activity and efficient VNB incorporation.

We used this catalyst to explore the effect of various reaction parameters like Al/Ti molar ratio, reaction time and temperature on copolymerization behaviour. As summarized in Table 2, a certain excess amount of MMAO was required for exhibiting high catalytic activity (entries 9 and 10 vs. entries 11 and 12) in this catalyst system. In addition, the increase in Al/Ti molar ratio led to a decrease in the molecular weight of the copolymer, indicating that chain-transfer to aluminum alkyls is the dominant chain-transfer pathway in the E/VNB copolymerization under these conditions. The polymerization reactions proceeded at significant rates, especially at the initial stage and then decreased gradually, probably since the mass transport limitations could have occurred with this highly active catalyst (entries 9, 13 and 14 in Table 2). The maxmium activity of 9360 $\mathrm{kg\,mol^{-1}{}_{Ti}\cdot h}$ could be attained on a 5-min scale experiment. Neither the molecular weight value nor ENB incorporation changed with the time, which indicated that cross-linking by the insertion of the ethylidenyl group with another Ti-alkyl bond was not accomplished or was negligible under the conditions employed.[8c] A significant decrease in the activity and molecular weight was found if the copolymerization was conducted at 50 °C (entries 15 and 16 in Table 2), maybe due to the rapid deactivation of the catalyst. The level of VNB incorporation approached 40 mol% in the resultant copolymer.

The copolymer prepared by **1** and **5** displayed the similar structure, and no significant differences were observed in the ^{13}C NMR spectra. This fact strongly suggests that a similar catalytically active species plays a role in this copolymerization. The ^{1}H NMR spectra were consistent with the formation of thze true copolymer. The resonances at 5.1 and 5.3 ppm are to be assigned to the ethylidene norbornene olefinic residues. The absence of resonances at 6.25 ppm is an indication that ENB incorporates solely *via* its intracyclic unsaturation double bond. The same 4:1 mole ratio observed for the *E/Z* configurational isomers of the ENB monomer was also detected for the structures **2a** and **2b**.[10] This result indicates that both ENB isomers reacted with the same probability. Figure 2 shows the ^{13}C NMR spectrum of poly(E-*co*-ENB) (entry 10). Similar to the E/VNB copolymer, the microstructures of the copolymer produced by **2** possessed isolated ENB inserted units and an E/ENB alternating sequence. The resonances ascribed to repeated ENB insertion were not observed. These facts were also in line with the result of ethylene/norbornene (N) copolymerization, in which the copolymer with similar co-monomer incorporation consisted almost completely of isolated N sequences and alternating sequences in the absence of NN sequences. Species **6** gave bimodal MWDs polymers under the same conditions. This result clearly suggests that both the catalyst structure and monomer employed significantly influenced the polymerization performances.

Two non-conjugated cyclic dienes (VNB and ENB) were tested for the copolymerization with ethylene in the presence of bis(β-enaminoketonato)titanium catalysts. Either incorporation of VNB or ENB in polyethylene chains proceeds easily. Cross-linking was negligible during copolymerization with any of the catalysts examined. The diene incorporation, catalytic activity, the molecular weight of the resultant polymers not only depended on the catalyst and monomer employed but also on the experimental conditions. As far as we know, the present catalyst system is a rare example for affording high molecular weight polymers by polymerization with significant catalyst efficiency using non-Cp transition metal catalysts. However, we do not have an exact reason why a significant difference (catalytic activity, molecular weight, MWDs) can be observed among these catalysts. We are now exploring this in more detail, and results will be made available in the near future.

Experimental Section

General Procedure

All manipulations of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. VNB and ENB were purchased from Acros and stored in a bottle in the drybox in the presence of molecular sieves. 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. Complexes **1–6** were synthesized according to the procedure reported previously.[9b]

Gel permeation chromatographic (GPC) measurements were carried out on a Waters instrument (515 HPLC pump) equipped with a Wyatt interferometric refractometer, eluted with THF at 25 °C at 1 $\mathrm{mL\,min^{-1}}$. The molecular weights were calibrated against polystyrene standards. All ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si.

Copolymerization of Ethylene with VNB or ENB

Ethylene was copolymerized with VNB (or ENB) at 1 atm in a 200-mL Schlenk flask equipped with a mechanical stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with ethylene gas from a Schlenk line. Toluene, VNB (or ENB), and catalyst solution in toluene were added *via* a gastight syringe. At desired reaction temperature, the polymerization was initiated by the addition of a heptane solution of MMAO into the reactor with vigorous stirring. After a prescribed time, the reaction was quenched with ethanol containing 10% (v/v) hydrochloric acid, and the ethylene gas feed was stopped. The resulting product was added to acidic ethanol. The polymer was isolated by filtration, washed with ethanol, and dried at 60 °C for 12 h in a vacuum oven.

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References

[1] a) G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223–1252; b) M. J. Yanjarappa, S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347–1398; c) X. F. Li, Z. M. Hou, *Coord. Chem. Rev.* **2008**, *252*, 1842–1869; d) T. C. Chung, J. Y. Dong, *Macromolecules* **2002**, *35*, 2868–2870; e) K. Nomura, J. Y. Liu, M. Fujiki, A. Takemoto, *J. Am. Chem. Soc.* **2007**, *129*, 14170–14171.

[2] a) R. Mulhaupt, D. W. Ovenall, S. D. J. Ittel, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2487–2500; b) T. Tsujino, T. Saegusa, J. Furukawa, *Macromol. Chem.* **1965**, *85*, 71–79.

[3] a) W. Kaminsky, M. Schlobohm, *Makromol. Chem. Macromol. Symp.* **1986**, *4*, 103–118; b) W. Kaminsky, H. Drogemuller, *Makromol. Chem. Rapid Commun.* **1990**, *11*, 89–94.

[4] a) G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1991**, *113*, 6270–6271; b) G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1993**, *115*, 91–98; c) L. Cavallo, G. Guerra, P. Corradini, L. Resconi, R. M. Waymouth, *Macromolecules* **1993**, *26*, 260–267.

[5] a) N. Naga, T. Shiono, T. Ikeda, *Macromolecules* **1999**, *32*, 1348–1355; b) N. Naga, T. Shiono, T. Ikeda, *Macromol. Chem. Phys.* **1999**, *200*, 1466–1472; c) N. Naga, Y. Imanishi, *Macromol. Chem. Phys.* **2002**, *203*, 771–777; d) N. Naga, Y. Imanishi, *Macromol. Chem. Phys.* **2002**, *203*, 2155–2162.

[6] a) M. Marques, Z. Yu, M. D. Rausch, J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2787–2793; b) W. Kaminsky, D. Arrowsmith, H. R. Winkelbach, *Polym. Bull.* **1996**, *36*, 577–584; c) A. G. Simanke, R. S. Mauler, G. B. Galland, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 471–485; d) K. Radhak-

rishnan, S. Sivaram, *Macromol. Chem. Phys.* **1999**, *200*, 858–862; e) K. Mönkkönen, T. T. Pakkanen, *Macromol. Chem. Phys.* **1999**, *200*, 2623–2628; f) J. Suzuki, Y. Kino, T. Uozumi, T. Sano, T. Teranishi, J. Jin, K. Soga, T. Shiono, *J. Appl. Polym. Sci.* **1999**, *72*, 103–108; g) N. Naga, G. Tsuchiya, A. Toyota, *Polymer* **2006**, *47*, 520–526.

[7] a) S. Marathe, S. Sivaram, *Macromolecules* **1994**, *27*, 1083–1086; b) I. Kim, *React. Funct. Polym.* **2001**, *49*, 197–204; c) H. Lasarov, T. T. Pakkanen, *Macromol. Chem. Phys.* **2000**, *201*, 1780–1786; d) H. Lasarov, T. T. Pakkanen, *Macromol. Rapid Commun.* **1999**, *20*, 356–360; e) H. Lasarov, T. T. Pakkanene, *Macromol. Rapid Commun.* **2001**, *22*, 434–438; f) T. Hasan, T. Ikeda, T. Shiono, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4581–4587; g) J. C. W. Chien, D. He, *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1609–1613.

[8] a) D. E. Heiser, F. Pelascini, D. Kramer, J. Scott, S. Gambarotta, J. McCahill, D. W. Stephan, J. Okuda, R. Mülhaupt, *Macromol. Symp.* **2006**, *236*, 156–160; b) D. E. Heiser, J. Okuda, S. Gambarotta, R. Mülhaupt, *Macromol. Chem. Phys.* **2005**, *206*, 195–202; c) N. Naga, *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 1285–1291; d) H. C. Li, J. C. Li, Y. T. Zhang, Y. Mu, *Polymer* **2008**, *49*, 2839–2844; e) N. Bavarian, M. C. Baird, J. S. Parent, *Macromol. Chem. Phys.* **2001**, *202*, 3248–3252.

[9] a) L. Pan, W. P. Ye, J. Y. Liu, M. Hong, Y. S. Li, *Macromolecules* **2008**, *41*, 2981–2983; b) X. F. Li, K. Dai, W. P. Ye, L. Pan, Y. S. Li, *Organometallics* **2004**, *23*, 1223–1230; c) L. M. Tang, Y. Q. Duan, L. Pan, Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1681–1689.

[10] G. Suzukamo, M. Fukao, M. Minobe, *Chem. Lett.* **1987**, 585–588.