Living Copolymerization of Ethylene with Norbornene Catalyzed by Bis(Pyrrolide−Imine) Titanium Complexes with MAO

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Abstract: Bis(pyrrolide−imine) Ti complexes in conjunction with methylalumoxane (MAO) were found to work as efficient catalysts for the copolymerization of ethylene and norbornene to afford unique copolymers via an addition-type polymerization mechanism. The catalysts exhibited very high norbornene incorporation, superior to that obtained with $Me_2Si(Me_4Cp)(N\text{-}tert\text{-}Bu)TiCl_2$ (CGC). The sterically open and highly electrophilic nature of the catalysts is probably responsible for the excellent norbornene incorporation. The catalysts displayed a marked tendency to produce alternating copolymers, which have stereoirregular structures despite the C_2 symmetric nature of the catalysts. The norbornene/ethylene molar ratio in the polymerization medium had a profound influence on the molecular weight distribution of the resulting copolymer. At norbornene/ethylene ratios larger than ca. 1, the catalysts mediated room-temperature living copolymerization of ethylene and norbornene to form high molecular weight monodisperse copolymers ($M_n > 500\,000$, $M_w/M_n < 1.20$). ^{13}C NMR spectroscopic analysis of a copolymer, produced under conditions that gave low molecular weight, demonstrated that the copolymerization is initiated by norbornene insertion and that the catalyst mostly exists as a norbornene-last-inserted species under living conditions. Polymerization behavior coupled with DFT calculations suggested that the highly controlled living polymerization stems from the fact that the catalysts possess high affinity and high incorporation ability for norbornene as well as the characteristics of a living ethylene polymerization though under limited conditions (M_n 225 000, M_w/M_n 1.15, 10-s polymerization, 25 °C). With the catalyst, unique block copolymers [i.e., poly(ethylene-*co*-norbornene)$_1$-*b*-poly(ethylene-*co*-norbornene)$_2$, PE-*b*-poly(ethylene-*co*-norbornene)] were successfully synthesized from ethylene and norbornene. Transmission electron microscopy (TEM) indicated that the PE-*b*-poly(ethylene-*co*-norbornene) possesses high potential as a new material consisting of crystalline and amorphous segments which are chemically linked.

Introduction

Making polymers with precise control over molecular weight, composition and architecture of the polymer (precisely controlled polymers) has been a long-standing challenge in the field of polymer chemistry. Living olefin polymerization is one of the most useful tools for the synthesis of precisely controlled polymers such as monodisperse polymers, terminally functionalized polymers, and block copolymers. These polymers are expected to display unique material properties that have not been achieved by conventional polymers.

Recent advances in the rational design and synthesis of well-defined transition metal complex catalysts for olefin polymerization[1] have resulted in the discovery and development of quite a few efficient and selective catalysts for the living polymerization of ethylene, propylene, 1-hexene, or other olefins.[2−5] These catalysts have enabled us to prepare a wide array of living-polymerization-based polymers, which include high molecular weight monodisperse polyethylenes (PEs), highly syndiotactic polypropylenes (sPPs), highly isotactic poly(1-hexene)s (iPHs), and a variety of block copolymers from ethylene and α-olefins [PE-*b*-poly(ethylene-*co*-propylene), sPP-*b*-poly(ethylene-*co*-propylene), iPP-*b*-PE, PE-*b*-poly(ethylene-*co*-1-octadecene)].[6,7]

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(2) For a recent review, see: Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257. For living olefin polymerization with phenoxy-based catalysts, see ref 1f.

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Compared with ethylene and/or common α-olefin (co)-polymerizations, ethylene (E)/norbornene (NB) copolymerizations have been investigated less despite the importance of the resultant copolymers in various fields due to their remarkable material properties (e.g., high thermal stability, high transparency, high refractive indices).[8−11] Therefore, there are only a few examples of catalysts that copolymerize E and NB in a

(quasi) living fashion.[12] Such catalysts are *rac*-Et(Ind)₂ZrCl₂/ methylalumoxane (MAO) and Me₂Si(Me₄Cp)(*N-tert*-Bu)TiCl₂/ MAO as reported by Tritto and co-workers.[12b−d] In addition, there exists only one recent report, and that is by Li et al. on the synthesis of E- and NB-based block copolymers using bis-(β-enaminoketonato) Ti complexes,[12e] which should display distinctive properties and thus may have expanded utility. Hence, the development of catalysts for living copolymerization of E and NB is a comparatively uncharted field though the development would have an impact on catalyst chemistry and polymer chemistry.

In our study, we have performed research into the ligand-oriented design of catalysts in order to acquire high-performance olefin polymerization catalysts.[3d,e,4b,6b,13−15] As a consequence, we have developed bis(pyrrolide−imine) Ti complexes (named PI Catalysts)[16,17] that were discovered as a result of the combination of electronically flexible nonsymmetric [N⁻, N] chelate ligands and group 4 transition metals.[18] PI Catalysts combined with MAO display high ethylene polymerization activities comparable to those seen with early metallocene catalysts. In addition, PI Catalysts in conjunction with *i*Bu₃Al/ Ph₃CB(C₆F₅)₄ form ultrahigh molecular weight polyethylenes. Moreover, we found that PI Catalysts with MAO can carry out

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Table 1. E/NB Copolymerization Results[a]

entry	complex	NB[b] (g)	NB/E molar ratio	yield (mg)	activity[c]	$M_n{}^d$ ($\times 10^3$)	$M_w/M_n{}^d$	NB content[e] (mol %)
1	**1**	1	0.34/1	356	4272	652	1.28	26.5
2	**1**	10	3.4/1	206	2472	285	1.11	45.0
3	*rac*-Et(Ind)$_2$ZrCl$_2$	1	0.34/1	591	7092	126	1.95	8.3
4	Me$_2$Si(Me$_4$Cp)(N-*tert*-Bu)TiCl$_2$	1	0.34/1	0	0			
5	Me$_2$Si(Me$_4$Cp)(N-*tert*-Bu)TiCl$_2$	10	3.4/1	1280	15 360	858	4.66	31.2

[a] Conditions: 25 °C, 5 min, atmospheric pressure, E gas feed (50 L/h). Complex: 1 μmol, cocatalyst; MAO 1.25 mmol as Al (entries 1−4), ^{i}Bu$_3$Al 0.25 mmol, Ph$_3$CB(C$_6$F$_5$)$_4$ 6 μmol (entry 5), toluene 250 mL. [b] Charged NB. [c] kg-polymer/mol-cat/h. [d] Determined by GPC, equipped with refractive index (RI) detector, by using polystyrene calibration. [e] Determined by ^{13}C NMR.

Scheme 1. Synthetic Procedure for Complexes **1**−**4**
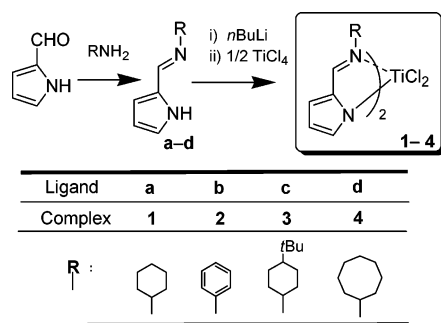
living E/NB copolymerization at room temperature and produce high molecular weight monodisperse alternating copolymers. In this contribution, we describe the detailed E/NB copolymerization behavior of PI Catalysts and discuss the mechanism of the living copolymerization. Additionally, we introduce the preparation of E- and NB-based block copolymers with unique architectures using PI Catalysts. The results discussed herein would provide a new strategy for achieving highly controlled living copolymerization of ethylene with strained cyclic olefins.

Results and Discussion

Synthesis of Bis(Pyrrolide−Imine) Ti Complexes. The synthetic route used to prepare the titanium complexes utilized in this work is depicted in Scheme 1. Complexes **1** and **2** were synthesized and purified according to previously reported procedures.[17b] Complexes **3** and **4** were prepared from TiCl$_4$ and the lithium salts of the corresponding pyrrolide-imine ligands using a similar method. The desired complexes were obtained in moderate to good overall yields from pyrrole-2-carboxaldehyde (**1**, 36%; **2**, 51%; **3**, 55%; **4**, 41%).

Ethylene/Norbornene Copolymerization Promoted by the Complexes 1−4/MAO Systems. Using MAO as a cocatalyst E/NB copolymerizations with complex **1** and two metallocenes [i.e., *rac*-Et(Ind)$_2$ZrCl$_2$ and Me$_2$Si(Me$_4$Cp)(N-*tert*-Bu)TiCl$_2$ (CGC)], for comparison, were carried out at 25 °C under atmospheric pressure. Polymer yields, polymerization activities, M_n, M_w/M_n, and NB contents of the resulting polymers are reported in Table 1.[19] Although complex **1**/MAO displayed somewhat lower (but still respectable) activity (entry 1, 4272

kg-polymer/mol-cat/h) for the polymerization, it produced higher molecular weight polymer with higher NB content (M_n 652 000, NB content 26.5 mol %) than *rac*-Et(Ind)$_2$ZrCl$_2$ with MAO (M_n 126 000, NB content 8.3 mol %). Under the conditions employed, CGC/MAO exhibited practically no reactivity toward the polymerization, and neither oligomeric nor polymeric materials were isolated.[20] Since CGC often shows higher catalytic properties on activation with a borate cocatalyst than with MAO,[1b] we also performed E/NB copolymerization with CGC/^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$. The CGC system produced copolymer having a NB content of 31.2 mol % with very high productivity (15 360 kg-polymer/mol-cat/h, entry 5). It is noteworthy that complex **1** formed a copolymer with higher NB content (45.0 mol %, entry 2) than CGC (31.2 mol %) which is well-known to display very high incorporation of sterically large monomers. Considering that NB is a sterically encumbered monomer and has higher nucleophilicity relative to common α-olefins, the high NB incorporation observed may be associated with the high electrophilicity and sterically open nature of the active site of complex **1**.[17c] DFT calculations[21] suggest that the Ti center of a cationic methyl species derived from complex **1** has higher electrophilicity (Mulliken charge of the Ti center in atomic units 1.84) than that from CGC (Mulliken charge of the Ti center in atomic units 1.69). The high electrophilicity may stem from the relatively low HOMO energy of a pyrrolide−imine ligand (e.g., pyrrolide−imine ligand of complex **1**; HOMO −3.21 eV, Cp ligand; HOMO −2.33 eV, calculated by PM3 method[22]).

It is significant to note that the copolymers arising from complex **1**/MAO possess very narrow molecular weight distributions (M_w/M_n: entry 1, 1.28; entry 2, 1.11). These M_w/M_n values suggested that the complex **1** catalyst system may have the characteristics of a living E/NB copolymerization. While *rac*-Et(Ind)$_2$ZrCl$_2$/MAO was not able to produce narrow molecular weight distribution copolymer (M_w/M_n 1.95) under the conditions examined (NB/E molar ratio 0.34/1), Tritto et al.

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(19) NB/E molar ratio in a polymerization medium was calculated based on the literature data under the assumption that the toluene is saturated with E during the course of the polymerization and that NB consumption is negligible for the polymerization. See: Sernetz, F. G.; Mülhaupt, R.; Waymouth, R. M. *Macromol. Chem. Phys.* **1996**, *197*, 1071−1083.

(20) With CGC/MAO at 50 °C, Tritto et al. obtained an E−NB copolymer having a narrow molecular weight distribution of 1.3 (M_n 100 000) with low efficiency.[12c] Details of the polymerization conditions are not given.

(21) (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967. (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391−403. (c) ADF2003.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (e) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (f) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *175*, 200−206. (g) Vanka, K.; Xu, Z.; Ziegler, T. *Organometallics* **2004**, *23*, 2900−2910. (h) Kim, E. G.; Klein, M. L. *Organometallics* **2004**, *23*, 3319−3326.

(22) PM3 calculations were carried out using Spartan '02 program, Wavefunction, Inc., Irvine, CA. See: Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220, 221−264.

Table 2. E/NB Copolymerization Results with Complexes
1−**4**/MAO[a]

| entry	complex	NB[b] (g)	time (min)	yield (mg)	activity[c]	M_n[d] ($\times 10^3$)	M_w/M_n[d]	T_g[e] (°C)
1	**1**	10	1	54	3240	74	1.07	116
2	**1**	10	3	143	2860	179	1.11	118
3	**1**	10	5	206	2472	285	1.11	118
4	**1**	10	10	455	2730	521	1.16	120
5	**2**	10	5	45	540	72	1.08	126
6	**2**	10	10	96	576	127	1.10	130
7	**2**	10	20	176	528	229	1.15	132
8	**3**	10	1	38	2280	61	1.08	120
9	**3**	10	3	110	2200	177	1.10	120
10	**3**	10	5	186	2232	239	1.14	120
11	**3**	10	10	359	2154	417	1.24	121
12	**4**	10	1	56	3360	81	1.09	124
13	**4**	10	3	166	3320	237	1.14	124
14	**4**	10	5	273	3276	344	1.18	124
15	**4**	10	10	531	3186	600	1.23	126

[a] Conditions: 25 °C, atmospheric pressure, E gas feed (50 L/h).
Complex: 1 μmol, cocatalyst; MAO 1.25 mmol as Al, toluene 250 mL.
[b] Charged NB. [c] kg-polymer/mol-cat/h. [d] Determined by GPC, equipped
with refractive index (RI) detector, by using polystyrene calibration.
[e] Measured by DSC.
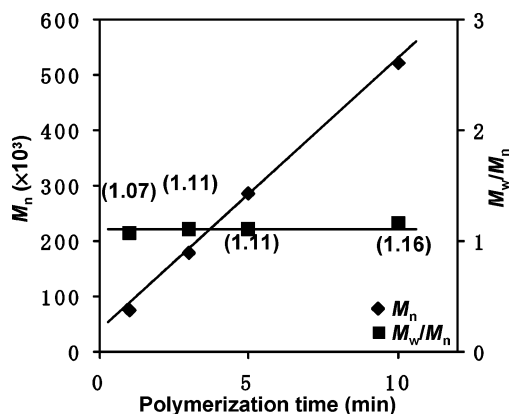
Figure 1. Plots of M_n and M_w/M_n vs polymerization time with complex
1/MAO.

achieved a quasi-living copolymerization with this catalyst
system at a high NB/E molar ratio of 28.4/1 (M_n 133 000, M_w/M_n 1.16, activity 920 kg-polymer/mol-cat/h).[12b,d]

In an attempt to confirm the living nature of the complex **1**
catalyst system, M_n and M_w/M_n values were monitored as a
function of polymerization time (entries 1−4 in Table 2). For
each run, a similar glass transition temperature (T_g 116−120
°C), (T_g correlates with NB content),[9j,10d] and thus a similar
NB content copolymer was obtained, indicating that the po-
lymerization proceeded at practically the same NB/E molar ratio
under the conditions employed (calculated NB conversion <
5%). A plot of M_n and M_w/M_n values vs polymerization time is
shown in Figure 1. The M_n value increased proportionally with
polymerization time, and the narrow M_w/M_n value was retained
for each run (M_w/M_n 1.07−1.16), suggesting that the system is
indeed living. GPC peaks of the produced copolymers shifted
to the higher molecular weight region with an increase in
polymerization time while the unimodal shape was maintained
and no shoulder peak and/or no low molecular weight tail was
detected during the course of the polymerization (Figure 2).
These results clearly indicate that the complex **1** catalyst system
initiates highly controlled living E/NB copolymerization.

To obtain further information about the E/NB copolymeri-
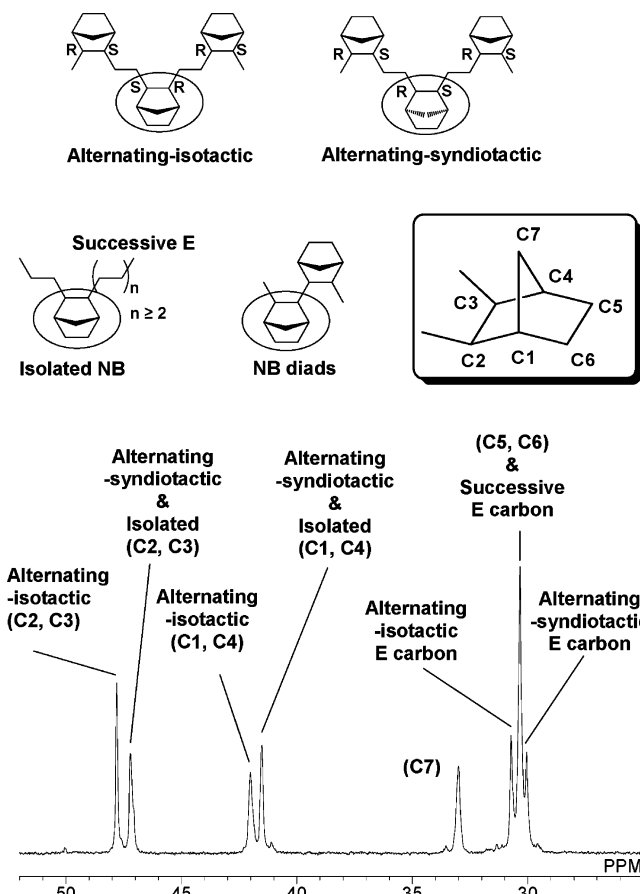zation behavior of bis(pyrrolide−imine) Ti complexes, com-
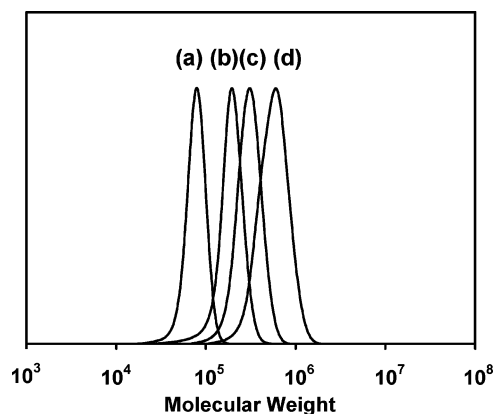
Figure 2. GPC profile of the E-NB copolymer formed with complex
1/MAO: (a) 1 min, M_n 74 000, M_w/M_n 1.07; (b) 3 min, M_n 179 000, M_w/M_n 1.11; (c) 5 min, M_n 285 000, M_w/M_n 1.11; (d) 10 min, M_n 521 000,
M_w/M_n 1.16.

plexes **2**−**4** that possess different substituents on the imine-
nitrogens (R: **2**, Ph; **3**, 4-*tert*-butylcyclohexyl; **4**, cyclooctyl)
were also investigated for their potential as E/NB copolymer-
ization catalysts (entries 5−15 in Table 2).[23] These complexes
were found to form amorphous copolymers having very narrow
molecular weight distributions and high T_gs (**2**, M_w/M_n 1.08−
1.15, T_g 126−132 °C; **3**, M_w/M_n 1.08−1.24, T_g 120−121 °C;
4, M_w/M_n 1.09−1.23; T_g 124−126 °C) with high efficiency (**2**,
540−576 kg-polymer/mol-cat/h; **3**, 2154−2280 kg-polymer/
mol-cat/h; **4**, 3186−3360 kg-polymer/mol-cat/h). The living
nature of the complexes **2**−**4**/MAO systems was indicated by
the linear relationship between M_n and polymerization time as
well as by the narrow molecular weight distributions observed
(see the Supporting Information). Judging from the T_g values
of the resulting copolymers, we believe complexes **1**−**4** have a
similar ability to incorporate NB, which is substantially higher
than that of CGC under the given conditions.

**Microstructure of the E-NB Copolymer Produced with
the Complex 1/MAO System.** Figure 3 displays the ^{13}C NMR
spectrum of the living copolymer formed with complex **1** (M_n
285 000, M_w/M_n 1.11, entry 2 in Table 1). Peak assignments
were performed based on a comparison of the observed chemical
shifts with the literature data.[11c] The spectrum indicated that
complex **1** in conjunction with MAO promoted an addition-
type polymerization of NB, which is *exo-exo* enchained as
indicated by the presence of the peak at 33.0 ppm derived from
the C7 of NB (*exo-exo* enchainment) and the absence of the
peaks in the region of 36−37 ppm attributed to the C7 of NB
with *endo-endo* or *endo-exo* enchainment.[9j]

The peak at 47.8 ppm and the peaks in the region of 46.8−
47.4 ppm are assigned to C2 and C3 in the alternating isotactic
units and to C2 and C3 in the alternating syndiotactic units and
in the isolated units, respectively. The peaks in the region of
41.9−42.1 ppm are ascribed to C1 and C4 in the alternating
isotactic units, and those in the region of 41.4−41.7 ppm are
assignable to C1 and C4 in the alternating syndiotactic units
and in the isolated units. Additionally, the peak at 30.4 ppm is
attributed to C5, C6 and the carbons derived from successive E
enchainment. The peaks at 30.8 ppm and at 30.1 ppm are

(23) Complex **4** displayed a very high E polymerization activity of 33 200 kg-
PE/mol-cat/h, which exceeds those for early group 4 metallocenes (Cp$_2$-
TiCl$_2$; 16 700 kg-PE/mol-cat/h, Cp$_2$ZrCl$_2$; 20 000 kg-PE/mol-cat/h) under
identical conditions.

Figure 3. ^{13}C NMR spectrum for the living E-NB copolymer formed with complex **1** (entry 2 in Table 1).

Table 3. E or NB Homopolymerization and E/NB Copolymerization with Complex **1**/MAO[a]

entry	NB[b] (g)	time (min)	gas E/N$_2$ (L/h)/(L/h)	yield (mg)	activity[c]	M_n[d] (× 10³)	M_w/M_n[d]
1	0	5	2/100	11	132	94	2.10
2	0	$^1/_6$	50/0	87	(31 320)	225	1.15
3	0	0.5	50/0	195	(23 400)	429	1.38
4	10	20	0/50	0	0		
5[e]	10	20 + 10	0/50+50/0	220	(440)	338	1.29

[a] Conditions: 25 °C, atmospheric pressure, complex **1**: 1 μmol, cocatalyst; MAO 1.25 mmol as Al, toluene 250 mL. [b] Charged NB. [c] kg-polymer/mol-cat/h. [d] Determined by GPC, equipped with refractive index (RI) detector, by using polystyrene calibration. [e] After the treatment of **1**/MAO and NB for 20 min, E gas was introduced into the resulting mixture.

The catalyst system provided PE having an M_w/M_n of 2.10, indicating that complex **1** with MAO does not initiate living E polymerization under the given conditions. Interestingly, the catalyst system was found to produce a high molecular weight PE with a very narrow molecular weight distribution (M_n 225 000, M_w/M_n 1.15) in a short polymerization time of 10 s though the molecular weight distribution was somewhat broadened for 30-s polymerization (M_n 429 000, M_w/M_n 1.38). These results show that complex **1**/MAO possesses some characteristics of a living E polymerization and chain growth can occur without significant chain transfer or termination for a short time polymerization. The molecular weight and molecular weight distribution that were attained suggest a very high ratio of the rates of propagation to chain transfer for E polymerization with the catalyst system.

In contrast, complex **1**/MAO was found to show practically no reactivity toward NB homopolymerization, and neither oligomeric nor polymeric materials were isolated (entry 4). This result is consistent with the very high propensity of the catalyst system to afford alternating copolymers.

The living copolymerization catalysis displayed by **1**/MAO is unique since the catalyst system initiates neither E nor NB living polymerization under analogous conditions. Interestingly, though treatment of the catalyst system (**1**/MAO) with NB at 25 °C for 20 min formed neither polymeric nor oligomeric products, subsequent addition of E (50 L/h, 10 min) to the resulting mixture produced a high molecular weight copolymer having a narrow molecular weight distribution (M_n 338 000, M_w/M_n 1.29, entry 5) with a reasonable polymer yield (220 mg). This fact indicates that a catalytically active species is fairly stable under the conditions where no insertion of monomers occurs for 20 min.[24]

Effect of the Norbornene/Ethylene Ratio on the Copolymerization. Table 4 contains the results obtained for the copolymerization using **1**/MAO as a function of the amount of NB charged at 25 °C. As the charged NB increased (and thereby NB/E molar ratio increased), both the catalytic activity and the product molecular weight decreased. Although increasing the charged NB raised the incorporation of NB in the copolymer, the NB content in the copolymer reached a plateau value of ca. 50 mol %. Therefore, the decrease in the catalytic activity and the product molecular weight may be due to the predominant coordination of NB to an NB-last-inserted active species.

assigned to the carbons derived from E in the alternating isotactic units and those in the alternating syndiotactic units, respectively.

The relative peak intensities show that, though the copolymer contains 45.0 mol % of NB, it predominantly consists of alternating E−NB blocks [alternating sequence (−NB−E−*NB*−E−NB−), 95.4%]. In addition, the copolymer contains some isolated NB units present in PE sequence [isolated sequence (−E−*NB*−(E)$_n$−, $n \geq 2$, 3.7%] and only a small amount of NB diads (0.9%). These results suggest that complex **1**/MAO displays a very high tendency to afford alternating E-NB copolymers. Although NB can coordinate to a NB-last-inserted species (which will be discussed later), steric congestion associated with the insertion of NB to a Ti−norbornyl linkage probably disfavors successive NB enchainment. The relative peak intensities also reveal that the copolymer consists of about 48/52 of syndiotactic/isotactic units, indicating that the E-NB copolymer adopts an −NB−E−NB−E−NB− sequence with practically random tacticity. These facts suggest that an E-last-inserted active species cannot distinguish between coordination of NB with a bridging methylene group up or down though precatalyst complex **1** possesses C_2 symmetry. The sterically open nature of the active site may be related to the low degree of polymerization stereocontrol. The living copolymers stemming from complexes **2**−**4**/MAO possess virtually the same microstructures as that obtained with complex **1**/MAO.

Ethylene and Norbornene Homopolymerization with the Complex 1/MAO System. Table 3 summarizes the results of the homopolymerization of E and NB using complex **1**/MAO.

(24) The NB coordination to the cationic active species might play a role in the suppression of catalyst decay as a consequence of the steric protection to active site and the reduction of electrophilicity of the Ti center.

Table 4. E/NB Copolymerization Results with Complex **1**/MAO[a]

entry	NB[b] (g)	NB/E molar ratio	yield (mg)	activity[c]	M_n[d] (× 10³)	M_w/M_n[d]	NB content[e] (mol %)
1	0.5	0.17/1	2043	12 258	1998[f]	1.86[f]	
2	1	0.34/1	1343	8058	1078	1.46	22.2
3	5	1.7/1	684	4104	732	1.18	37.5
4	10	3.4/1	455	2730	521	1.16	44.5
5	20	6.8/1	217	1302	295	1.16	46.5
6	0	0/1	18	108	377	2.47	0

[a] Conditions: 25 °C, 10 min, atmospheric pressure. Entries 1−5: E (50 L/h). Entry 6: ethylene (5 L/h)/nitrogen (50 L/h). Complex **1**: 1 μmol, cocatalyst; MAO 1.25 mmol as Al, toluene 250 mL. [b] Charged NB. [c] kg-polymer/mol-cat/h. [d] Determined by GPC, equipped with refractive index (RI) detector, by using polystyrene calibration. [e] Determined by ¹³C NMR. [f] Soluble part in solvent under the measurement conditions.
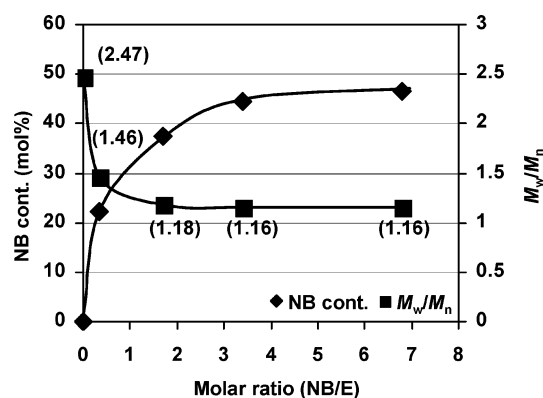
Figure 4. Plots of NB content and M_w/M_n vs NB/E molar ratio with complex **1**/MAO.

The most dramatic change observed is in the molecular weight distribution of the resultant copolymer. The plots of the NB content and M_w/M_n value of the resultant polymer vs NB/E molar ratio in a polymerization medium are shown in Figure 4. The NB/E molar ratio (and thus NB content of the resulting copolymer) significantly affects the molecular weight distribution; i.e., the catalyst system formed very narrow molecular weight distribution polymers under the conditions where the NB/E molar ratio is larger than 1, whereas the smaller NB/E molar ratio resulted in the production of broader molecular weight distribution polymers. It seems that an NB content of larger than ca. 30 mol % is a requirement for producing narrow molecular weight distribution copolymers in the present system.

Chain-End Analysis of the Copolymer. Chain-end analysis of a low molecular weight living copolymer using ¹³C NMR spectroscopy was performed in order to obtain further information about the copolymerization. Figure 5 shows the ¹³C NMR spectrum of the low molecular weight copolymer stemming from **1**/MAO (M_n 1800, M_w/M_n 1.16, NB content 50.8 mol %).[25] When the fact that the living copolymer (entry 3 in Table 1) contains a very small amount of NB−NB units is taken into account, chain-end structures which should be considered for the copolymer are CH₃−E−E−, CH₃−E−NB−, CH₃−NB− E− for the initiation chain ends and E−E−, E−NB−, NB− E− for the termination chain ends (see the Supporting Information).

(25) Polymerization conditions: complex **1** (200 μmol), MAO (10 mmol), E- and N₂- saturated toluene (250 mL, E 50 L/h, N₂ 50 L/h), charged NB (10 g), 0 °C, 5 s.

If the polymerization starts with E insertion into the Ti− CH₃ bond of an initial active species generated from complex **1** and MAO, the resulting copolymer possesses CH₃−E−E− (CH₃ of *n*-pentyl group; ca. 14.1 ppm) and/or CH₃−E−NB− (CH₃ of *n*-propyl group; ca. 14.8 ppm). However, no peaks assignable to the methyl carbons of the chain-end structures CH₃−E−E− and CH₃−E−NB−[26] were detected in the NMR. In addition, no peaks derived from the *β*-methylene carbons of the chain-end structures of CH₃−E−E− and CH₃−E−NB− (ca. 20−23 ppm) were found in the NMR. Rather, the peak at 15.8 ppm is attributable to the methyl carbon of the chain-end structure CH₃−NB−.[26] Additionally, the peaks at 40.6, 41.0, and 45.0 ppm are assignable to C3, C4, and C2 originating from the CH₃−NB− chain end, respectively. Therefore, the polymerization is initiated by NB insertion, resulting in the formation of the initiation chain-end structure CH₃−NB−. This fact further confirms the high incorporation capability of the catalyst system for NB.

Regarding the termination chain-end structures, the peaks at 29.1, 35.4, 36.8, and 38.6 ppm are assigned to C5, 7, 4, and 3 derived from the NB−E− chain end, respectively. The other carbons derived from the NB−E− chain end (C1, C2 and C6) are not assignable because of the overlap with the peaks originating from the main chain NB units. On the other hand, no peaks due to the E−E− (CH₃ of *n*-butyl group; ca. 12.1 ppm) and the E−NB− (CH₃ of ethyl group; ca. 12.0−14.0 ppm) were found in the NMR. These facts show that the catalytically active species mostly exists as a NB-last-inserted compound during the course of the polymerization. These results suggest that the NB insertion into the E-last-inserted species is much faster than the E insertion into the NB-last-inserted species under the conditions employed.

Origin of the Living Copolymerization. A plausible polymerization mechanism for E/NB copolymerization with the bis(pyrrolide−imine)Ti complex/MAO system is presented in Scheme 2. The chain-end analysis suggests the initial formation of Ti−NB−CH₃ species (1). Considering that the catalyst system favors the production of an alternating copolymer, after the formation of (1), propagation predominantly occurs by the insertion of E followed by NB one after the other according to the sequence (A)−(B)−(C)−(D).

As Fink and co-workers described,[10d] an NB-last-inserted species (2) is fairly stable toward chain transfers because of the difficulty in *β*-H transfers, whereas an E-last-inserted species (4) may undergo relatively fast chain transfer.[27] Therefore, the achievement of the highly controlled living copolymerization is probably as a consequence of the stabilization of an E-last-inserted species (4) toward chain transfers and its smooth transformation to a chain-transfer-wise stable NB-last-inserted species (2).

Relative formation energies estimated by DFT calculations[21] indicate that a NB-coordinated E-last-inserted species (5) [the

(26) Peak assignments were performed based on a comparison of the observed chemical shifts with the literature data (*exo*-2-methylbicyclo[2.2.1]heptane, *exo*-2-ethylbicyclo[2.2.1]heptane) (Lippmaa, E.; Pehk, T.; Belikova, N. A.; Bobyleva, A. A.; Kalinichenko, N.; Ordubadi, M. D.; Platé, A. F. *Org. Magn. Reson.* **1976**, *8*, 74−78.) and with the chemical shifts of the synthesized authentic sample of *exo*-2-*n*-propylbicyclo[2.2.1]heptane.

(27) E/NB copolymerization with **1**/MAO at 90 °C for 1 min produced a broadened molecular weight distribution copolymer (M_n 13 800, M_w/M_n 1.86) that possesses a vinyl end group (which is derived from a *β*-H transfer from the last-inserted E unit). These facts probably indicate that an E-last-inserted species undergoes fast chain transfer relative to an NB-last-inserted species.
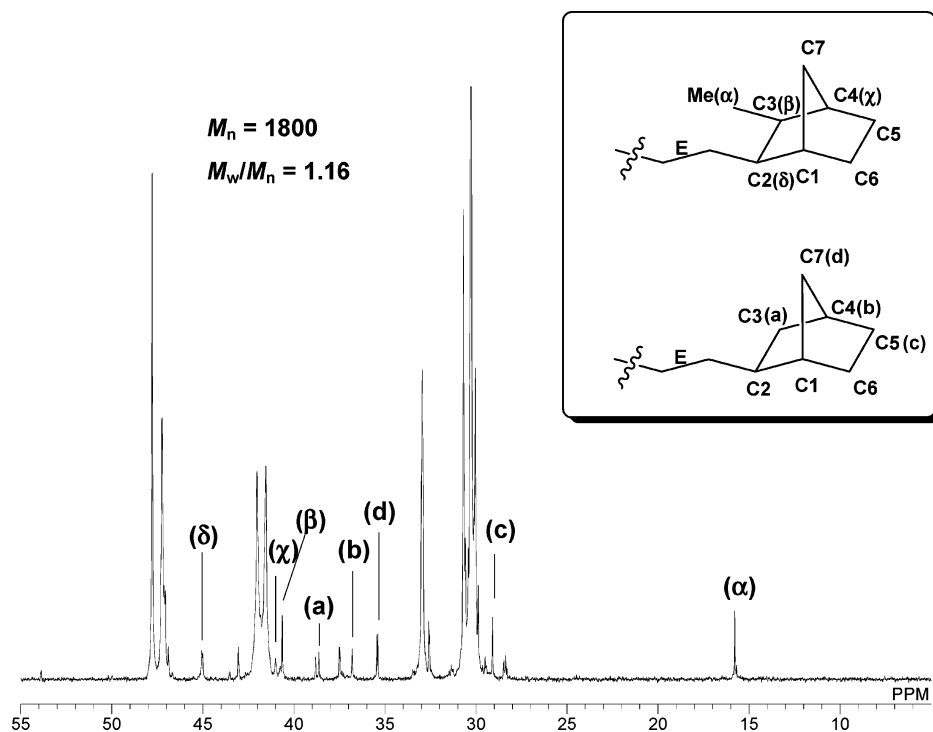
Figure 5. Chain-end analysis of the low molecular weight E-NB copolymer produced with complex **1**/MAO.

Scheme 2. Plausible Mechanism for Living E/NB Copolymerization Promoted by Complex **1**/MAO
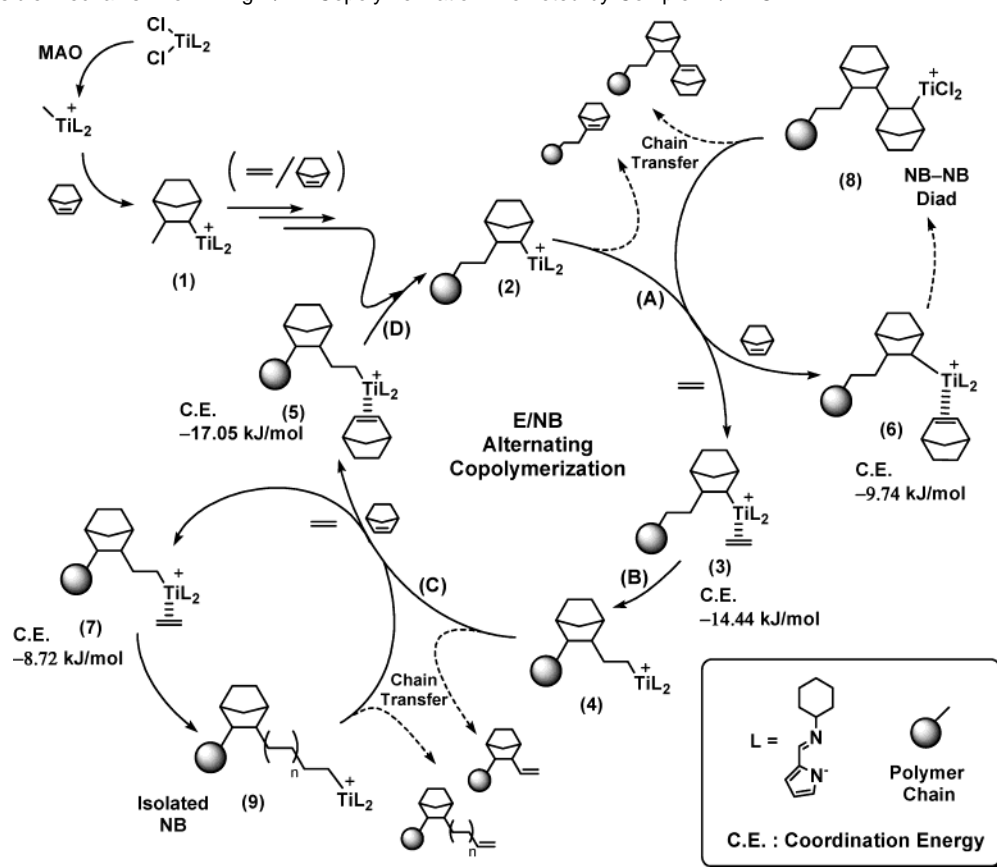
calculated structure is displayed in Figure 6(A)] is more stable than the corresponding E-coordinated species (7) by 8.33 kJ/mol, indicative of dominant NB coordination to the Ti center of the E-last-inserted species. The coordination of highly nucleophilic and sterically encumbered NB to the E-last-inserted

active species ((5), coordination energy; −17.05 kJ/mol) would reduce the electrophilicity of the active species and, in addition, provides steric congestion in close proximity to the active site, which probably mitigates chain transfers (e.g., β-hydrogen transfer to a reacting monomer, chain transfer to alkyl Al
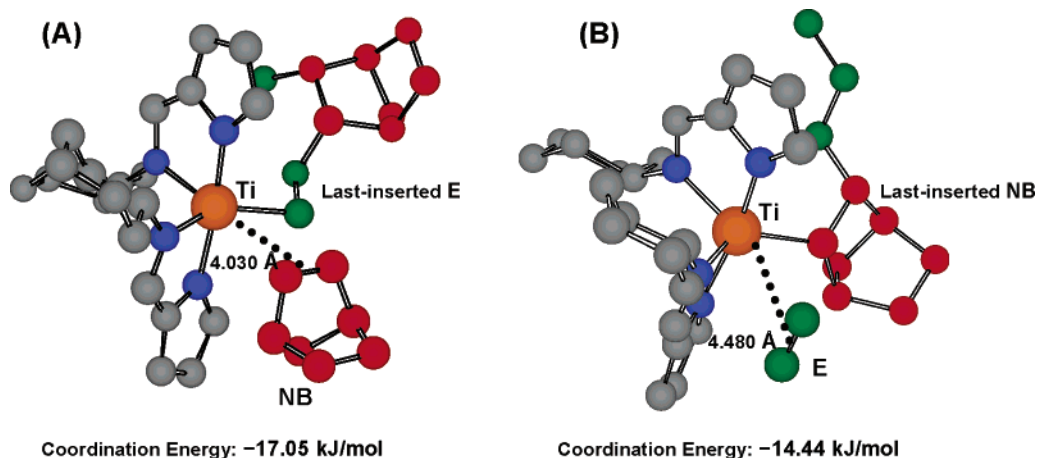
Figure 6. Calculated structures of an E-last-inserted species in the presence of NB ((5) in Scheme 2) and a NB-last-inserted species in the presence of E ((3) in Scheme 2).[28] Hydrogen atoms are omitted for clarity.

species). The facile insertion of NB to the E-last-inserted species was suggested by the fact that a growing polymer chain is detected exclusively as an NB-last-inserted state when the living copolymerization was quenched. The high NB affinity and the fast NB insertion are thought to arise from the sterically open and highly electrophilic nature of the active site.

Since the copolymers contain some isolated NB units present in the successive E units, reaction pathway (4)−(7)−(9) is also involved in the living copolymerization. As discussed, the catalyst system has characteristics of a living E polymerization though under limited conditions. The characteristics would allow the successive E enchainment without significant chain transfer with the E-NB copolymer exhibiting living character.

DFT calculations indicate that an E-coordinated species (3) [the calculated structure is shown in Figure 6(B)] is more stable than the NB-coordinated congener (6) by 5.70 kJ/mol, which may result in the formation of the NB−E sequence. Although the calculations suggest the preference of E coordination to an NB-last-inserted species (coordination energy; −14.44 kJ/mol), the coordination of NB to an NB-last-inserted propagating species (coordination energy; −9.74 kJ/mol) does not seem to be negligible considering the facts that increase in NB concentration in a polymerization medium results in a decrease in catalytic activity and that the copolymer contains NB−NB blocks though only a small amount. The NB coordination to the sterically hindered NB-last-inserted species presumably stems from the inherently high electrophilic characters of the active species.

On the basis of the above discussions, we concluded that the facile coordination of NB to the E-last-inserted species and its fast insertion to the species as well as the living character of E polymerization play key roles in the achievement of the highly controlled living copolymerization.[29]

(28) The distances between the coordinated NB and the Ti centers ((A) 4.030 Å, (B) 4.480 Å) are relatively large probably due to steric congestion stemming from the ultimately or penultimately inserted NB in the polymer chains.

(29) The quasi-living E/NB copolymerizations achieved by *rac*-Et(Ind)₂ZrCl₂ or Me₂Si(Me₄Cp)(*N-tert*-Bu)TiCl₂ with MAO are probably due to the enhancement of NB coordination to an E-last-inserted active species and the acceleration of NB insertion to the active species with the aid of a high NB concentration and, at the same time, a large excess of NB to E in a polymerization medium.

(30) We observed that PE (segment) was colored easily relative to poly(E-*co*-NB) (segment).
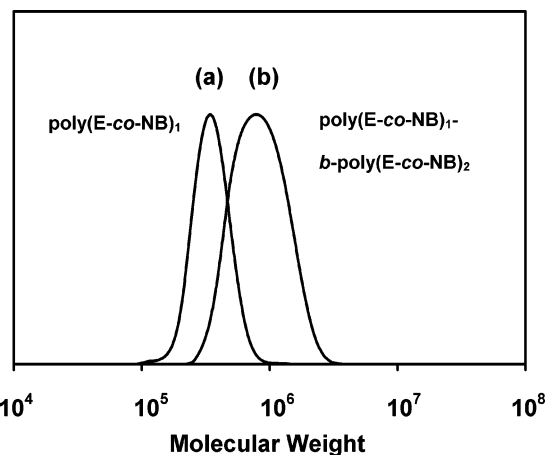
Figure 7. GPC profile of the poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂ formed with complex **1**/MAO: (a) prepolymer, M_n 329 000, M_w/M_n 1.11; (b) diblock copolymer, M_n 745 000, M_w/M_n 1.23.

Synthesis of Block Copolymers from Ethylene and Norbornene. Given the established living nature of E and E/NB (co)polymerizations with the bis(pyrrolide−imine) Ti complexes/MAO systems, we decided to explore the creation of E- and NB-based block copolymers, which consist of amorphous and amorphous or crystalline and amorphous segments.

Poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂ in which each copolymer segment contains a different NB content was prepared using E/NB toluene solutions. Treatment of **1** (1 μmol)/MAO (1.25 mmol) with E-saturated toluene (250 mL, E 50 L/h) containing NB (1 g) for 2 min with a continuous feed of E (50 L/h) resulted in the formation of the first poly(E-*co*-NB)₁ segment. Subsequent addition of NB (10 g) to the resulting mixture with the continuous E feed (50 L/h) formed a well-defined high molecular weight poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂. An overlay of the unimodal GPC elution curves for the first poly(E-*co*-NB)₁ (M_n 329 000, M_w/M_n 1.11, NB content 26.2 mol %) and the final poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂ (M_n 745 000, M_w/M_n 1.23, NB content 34.3 mol %) suggests a shift toward the higher molecular weight region due to the subsequent copolymerization step without providing any peak in the low-molecular weight region (Figure 7), demonstrating the creation of the target block copolymer. It is noteworthy that the block copolymer displays two sets of T_g's, 50 °C derived from the first segment (NB

Table 5. Synthesis of Various Block Copolymers Using Complex **1**/MAO[a]

	prepolymer					diblock copolymer					
entry	first block component	M_n^b (× 10³)	M_w/M_n^b	NB content[c] (mol %)	T_g^d (°C)	T_m^d (°C)	second block component	M_n^b (× 10³)	M_w/M_n^b	NB content[c] (mol %)	T_g^d (°C)	T_m^d (°C)
1	(E-*co*-NB)₁	329	1.11	26.2	52		(E-*co*-NB)₂	745	1.23	34.3	50, 119	
2	(E-*co*-NB)₃	406	1.28	19.5	20		(E-*co*-NB)₄	783	1.32	30.1	17, 123	
3	(E-*co*-NB)₅	223	1.38	7.6		88	(E-*co*-NB)₆	424	1.66	27.4	116	88
4	PE	119	1.34			134	(E-*co*-NB)₇	414	1.56	31.5	e	e

[a] Conditions: 25 °C, atmospheric pressure, E gas feed (50 L/h). Complex **1**: 1 μmol, cocatalyst; MAO 1.25 mmol as Al, toluene 250 mL. [b] M_n and M_w/M_n values were determined by GPC, equipped with refractive index (RI) detector (entries 1 and 2) and FT-IR detector (entries 3 and 4), by using polystyrene calibration. [c] Determined by ^{13}C NMR. [d] Measured by DSC. [e] Indistinguishable due to the overlap of T_g and T_m.

content 26.2 mol %) and 119 °C from the second segment (NB content 41.3 mol %, calculated from the polymer yields and NB contents of the first segment and the final block copolymer).

Likewise, two additional block copolymers, poly(E-*co*-NB)₃-*b*-poly(E-*co*-NB)₄ and poly(E-*co*-NB)₅-*b*-poly(E-*co*-NB)₆, were synthesized using different E/NB molar ratio toluene solutions. The poly(E-*co*-NB)₃-*b*-poly(E-*co*-NB)₄ block copolymer (the first segment; M_n 406 000, M_w/M_n 1.28, NB content 19.5 mol %, total; M_n 783 000, M_w/M_n 1.32, NB content 30.1 mol %) exhibits T_g's of 17 and 123 °C. Interestingly, the poly(E-*co*-NB)₅-*b*-poly(E-*co*-NB)₆ block copolymer (the first segment; M_n 223 000, M_w/M_n 1.38, NB content 7.6 mol %, total; M_n 424 000, M_w/M_n 1.66, NB content 27.4 mol %) displays both T_m (88 °C) due to the first crystalline segment and T_g (116 °C) associated with the second amorphous segment.

Moreover, a PE-*b*-poly(E-*co*-NB) diblock copolymer was also synthesized from E and NB by sequential monomer addition. Treatment of **1** (1 μmol)/MAO (1.25 mmol) with E- and N₂-saturated toluene (250 mL, E 50 L/h, N₂ 50 L/h) for 10 s with a continuous feed of E (50 L/h) and N₂ (50 L/h) (the first segment; M_n 119 000, M_w/M_n 1.34) and then addition of NB (10 g) to the resulting mixture and the halt of the N₂ feed produced a well-defined high molecular weight PE-*b*-poly(E-*co*-NB) block copolymer (M_n 414 000, M_w/M_n 1.56, NB content 31.5 mol %). A shift of GPC elution curves for the first PE segment and the final PE-*b*-poly(E-*co*-NB) toward the high-molecular-weight region suggests the formation of the block copolymer (see the Supporting Information). DSC measurements did not provide distinguishable T_g and T_m of the block copolymer because of the overlap of these temperatures.

Further information about the PE-*b*-poly(E-*co*-NB) block copolymer is given by transmission electron microscopy (TEM). The TEM micrograph of the press-sheet made of the PE/poly-(E-*co*-NB) blend polymer [Figure 8(A)] shows the grown lamellar structures of PE and the amorphous poly(E-*co*-NB) segment exists among the PE lamellar structures, while conversely that of the PE-*b*-poly(E-*co*-NB) [Figure 8(B)] displays considerable homogeneous structures. These results further confirm the formation of the desired block copolymer and, at the same time, demonstrate the high potential of the block copolymer as a new material composed of crystalline and amorphous segments that are chemically linked.

As disclosed in our patent[16b] filed on November 8, 2002, these are probably the first examples of the syntheses of E- and NB-based block copolymers. These unique block copolymers may be applied to a broad spectrum of applications that include compatibilizers, elastomers, and composite materials.
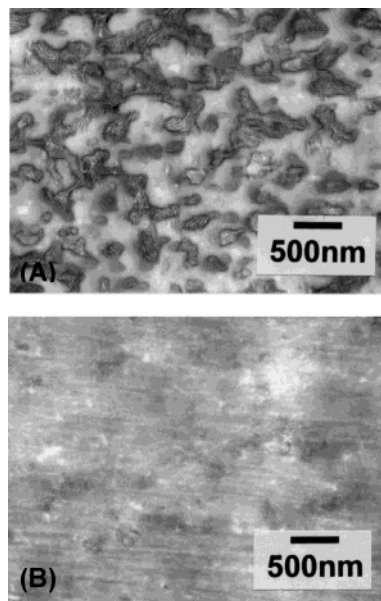
Figure 8. TEM micrographs of (A) PE and poly(E-*co*-NB) blend polymer (blend conditions: toluene, reflux temperature, 1 h) and (B) PE-*b*-poly(E-*co*-NB).[30]

Conclusions

In summary, the catalytic properties of bis(pyrrolide−imine) Ti complexes (PI Catalysts) for E/NB copolymerization have been described. PI Catalysts combined with MAO exhibit excellent NB incorporation, which exceeds that for Me₂Si(Me₄-Cp)(*N-tert*-Bu)TiCl₂ (CGC). The catalysts can mediate highly controlled room-temperature living E/NB copolymerization with a high propensity to form alternating copolymers. The catalyst systems can produce high molecular weight copolymers (M_n > 500 000, M_w/M_n < 1.2) and a number of block copolymers from E and NB [e.g., poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂, PE-*b*-poly-(E-*co*-NB)]. The highly controlled living copolymerization originates from the fact that the catalysts possess the high affinity and high incorporation ability for NB as well as some characteristics of a living E polymerization. The sterically open and highly electrophilic nature of the active species is probably responsible for the high affinity and high incorporation capability for NB. The achievement of the highly controlled living copolymerization by PI Catalysts with MAO may result in a new strategy for the development of high-performance catalysts for the living copolymerization of E and strained cyclic olefins. The results introduced herein together with our previous reports[17] suggest that PI Catalysts can exhibit unique polymerization behavior and thus have offered opportunities for the syntheses of distinctive polymers.

Supporting Information Available: Experimental section, DFT calculation results, plots of M_n and M_w/M_n vs polymerization time with complexes **2**−**4**/MAO for E/NB copolymerization, polymer analysis data (NMR, DSC, GPC, GC−MS), ^{13}C NMR data for 2-*n*-propylbicyclo[2.2.1]heptane, scheme for possible chain-end structures for an E-NB copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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