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Ethylene/Norbornene Copolymerization Behavior of Bis(phenoxy−imine)Ti Complexes Combined with MAO

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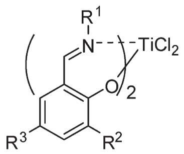
Polyolefins, as exemplified by polyethylene and polypropylene, display many useful properties, and hence they are used in the manufacture of numerous products, such as toys, bottles, pipes, packages, and a wide variety of automotive parts. Although the majority of commercially available polyolefins are still produced using heterogeneous, multi-sited Ziegler−Natta catalysts, single-site catalysts (as represented by group 4 metallocene catalysts) are becoming more prevalent in the marketplace.

Single-site catalysts have provided new opportunities for the syntheses of differentiated polymers from common olefinic feedstocks.[1,2] One example is the creation of well-defined ethylene (E)/norbornene (NB) copolymers using vanadium or group 4 metallocene catalysts. E/NB copolymers display high thermal stability and excellent optical properties that are imparted by the NB component, and they are thus used in heat-resistant and optical applications. Therefore, a great deal of academic and industrial research has been devoted to the efficient synthesis of E/NB copolymers with controlled macromolecular structures, making use of a variety of single-site catalysts.[3−5] These research projects have supplied useful insights into the relationship between catalyst structure vs NB incorporation capability and polymer microstructure.

As a result of ligand-oriented catalyst design research, we discovered the capabilities of bis(phenoxy−imine) and bis(phenoxy−ketimine) early transition metal complexes (now known as FI catalysts) for the controlled (co)polymerization of olefinic monomers.[6,7] When activated, FI catalysts can exhibit many unique features, including extremely high E selectivity relative to α-olefins, high functional group tolerance, and MAO- and borate-free polymerization catalysis.[8,9] Further research into FI catalysts has revealed a unique Ti-FI catalysis pathway for E/NB copolymerization. We therefore report on bis(phenoxy−imine)Ti complexes that are capable of achieving efficient NB coenchainment and which can afford (monodisperse) copolymers with high activity.

Figure 1 displays the bis(phenoxy−imine)Ti complexes (Ti-FI catalysts) **1**−**6** that were used in this study.[10,11] Electronically, NB is unique because it possesses a more nucleophilic nature than that possessed by the more common olefinic monomers such as E and propylene (P) [HOMO energy level, NB −7.25 eV, E −8.15 eV, P −7.66 eV; density functional theory (DFT) calculations]. Due to [O^-, N] heteroatom ligation, the catalytically active species derived from **1**−**6** probably possess higher electrophilicity than those species stemming from group 4 metallocene catalysts. These facts may suggest the high potential of these complexes for E/NB copolymerization.



	R^1	R^2	R^3
1	Ph	^{i}Pr	H
2	Ph	^{t}Bu	H
3	Ph	CMe_2Ph	Me
4	Ph	Me	H
5	Ph	Ph	H
6	*N*-pyrrolyl	Ph	H

Figure 1. Ti-FI catalysts used in this study.

The E/NB copolymerization behavior of complexes **1**−**6** was investigated in toluene with dried MAO (DMAO) activation.[12] The results are compiled in Table 1, which also includes the results obtained for $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ (CGC), *rac*-[Et(Ind)$_2$]ZrCl$_2$, and [Me$_2$C(Flu)(Cp)]ZrCl$_2$ for comparison.

Complexes **1**−**3** (R^2 = ^{i}Pr, ^{t}Bu, or CMe$_2$Ph) displayed no productivity under the conditions examined, yielding neither polymeric nor oligomeric products (Table 1, entries 1−3). The inactivity toward E/NB copolymerization is probably because there is insufficient space for the incorporation of the sterically encumbered NB, which is strongly bound to the highly electrophilic Ti center. In fact, complex **4**, which bears a sterically less encumbered methyl group at the R^2 position, produced a copolymer with a very high T_g of 120 °C (NB content 48.7 mol %; T_g correlates with NB content), displaying considerable activity (Table 1, entry 4).

Of particular note is the exceptional behavior of complexes **5** and **6**, which have a phenyl group at the R^2 position, and which achieve efficient NB coenchainment (high T_g's and high NB contents) and simultaneously high catalytic activity (Table 1, entries 5, 6 and 10, 11). These results demonstrate the beneficial effect of the phenyl group at the R^2 position on the incorporation of sterically hindered NB.[8b]

Notably, the copolymers arising from **5** (R^1 = Ph) and **6** (R^1 = pyrrolyl) possessed higher T_g's and NB contents than the copolymers obtained with CGC, *rac*-[Et(Ind)$_2$]ZrCl$_2$ or [Me$_2$C(Flu)(Cp)]ZrCl$_2$, which are known for achieving high NB incorporation.[4,5] These results indicate that **5** and **6** possess remarkably high incorporation ability for NB. Additionally, the catalytic performances (activity and NB incorporation) exhibited by complexes **5** and **6** with DMAO exceed those for bis(pyrrolide−imine)Ti complexes/DMAO and phenoxy−imine/pyrrolide−imine ligated Ti complexes/MAO.[4r,5d] In particular, complex **6,** which has a pyrrolyl group at the R^1 position, in combination with DMAO, is an exceptional catalyst for the copolymerization of E and NB because it displays significant E/NB copolymerization activity coupled with efficient NB coenchainment. In fact, complex **6**/DMAO is one of the best catalysts for E/NB copolymerization in terms of NB incorporation and catalyst efficiency.

Since the cationic methyl Ti species derived from complexes **5** and **6** have similar electrophilicity (Mulliken charge of the Ti in atomic unit: **5**, 1.762; **6**, 1.772), the higher activity exhibited by complex **6**/DMAO probably originates from its sterically less-encumbered active site compared with the activity from complex **5**/DMAO, due to the sterically smaller R^1 substituent. DFT calculations were performed on the NB-coordinated cationic Ti species (model; cationic *n*-propyl Ti complex) stemming from these complexes (Figure 2; NB−R^1 stands for the distance between the C atom of the olefinic moiety of the coordinated NB and the α-C

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Table 1. Ethylene/Norbornene Copolymerization Results[a]

entry	complex	yield/g	activity[b]	NB content[c]/mol %	T_g[d]/°C	M_w[e]/10^3	M_w/M_n[e]
1	**1**	0	0				
2	**2**	0	0				
3	**3**	0	0				
4	**4**	0.108	0.65	48.7	120	186	1.09
5	**5**	0.545	3.27	45.7	120	573	1.21
6	**6**[h]	0.582	6.98	46.1	126	215	1.91
7[f]	CGC[i]	0.400	4.80	25.8	47	2330	3.19
8	*rac*-[Et(Ind)$_2$]ZrCl$_2$	0.292	1.75	27.7	49	476	1.74
9	[Me$_2$C(Flu)(Cp)]ZrCl$_2$	0.234	1.40	28.0	49	259	1.58
10[f,g]	**5**	0.169	2.02	48.4	129	198	1.13
11[f,g]	**6**	0.419	5.03	48.9	133	293	1.87
12[f,g]	CGC[i]	0.276	3.31	33.6	65	653	2.14
13[g]	*rac*-[Et(Ind)$_2$]ZrCl$_2$	0.345	2.07	36.8	85	271	1.81
14[g]	[Me$_2$C(Flu)(Cp)]ZrCl$_2$	0.136	0.82	35.2	78	334	1.41

[a] Conditions: toluene 250 mL, complex 1.0 μmol charged norborene 5 g, 25 °C, 10 min, ethylene 0.1 MPa cocatalyst DMAO 1.25 mmol as Al. [b] kg of polymer/(mmol of cat·h). [c] Determined by ^{13}C NMR (see Supporting Information). [d] Measured by DSC. [e] Determined by GPC using polystyrene calibration. [f] Polymerization time 5 min. [g] Charged norbornene 10 g. [h] Complex 0.5 μmol. [i] Cocatalyst Ph$_3$ CB(C$_6$F$_5$)$_4$ 6 μmol, ^{i}Bu$_3$Al 0.25 mmol.

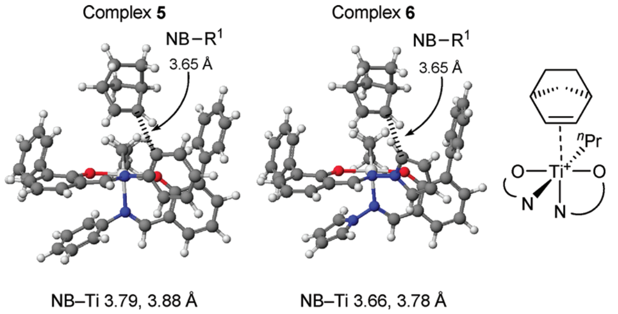

Figure 2. Calculated structures of NB-coordinated cationic *n*-propyl Ti species generated from complexes **5** and **6**.[7]

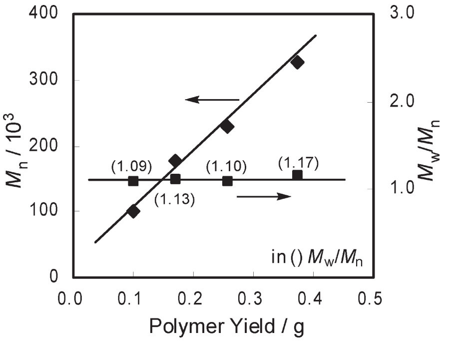

Figure 3. Plots of M_n and M_w/M_n as a function of polymer yield for E/NB copolymerization with complex **5**/DMAO (see Supporting Information).

atom of the R^1 substituent, and NB−Ti represents the distances between the Ti atom and the C atoms of the olefinic moiety of the coordinated NB). The results indicate that the nearest C atom on the ligand to the C atom on the coordinated NB (which is the C atom of the olefinic moiety of the coordinated NB) is the α-C atom of the R^1 substituent; the distance is 3.65 Å in both cases. Additionally, the calculations also suggest that the coordinated NB for the cationic species originating from complex **6** exists in closer proximity to the Ti metal (NB−Ti; **5** 3.79 and 3.88 Å, **6** 3.66 and 3.78 Å). These results indicate that the cationic species derived from complex **6** possess a sterically more open nature compared to those derived from complex **5**, which is consistent with the experimental results described above.

An inspection of the data in Table 1 (entries 5, 6 and 10, 11) shows that increasing the mol % of charged NB gave rise to no significant increase in the NB content. ^{13}C NMR microstructural analyses of the copolymers formed with complexes **5** (NB content 48.4 mol %; Table 1, entry 10) and **6** (NB content 48.9 mol %; Table 1, entry 11) revealed that these complexes have a very high propensity to produce alternating copolymers [**5**, −NB−E−NB−E−NB− 96.1%, −E−NB−(E)$_n$ 3.9%; **6**, −NB−E−NB−E−NB− 96.0%, −E−NB−(E)$_n$ 4.0%]. The ^{13}C NMR studies also showed that the copolymer made with complex **5** had a slightly syndiotactic-enriched structure (−NB−E−NB−: iso/syn 45/55) whereas the copolymer made with complex **6** possessed an isotactic-enriched structure (iso/syn 66/34). The origin of these differences in stereoselectivity for complexes **5** and **6** (both have a C_2 symmetric nature) is unclear at this time.[13]

GPC analyses demonstrated that, though the copolymer produced with complex **6** has an M_w/M_n value of 1.87 (Table 1, entry 11), the copolymer formed with complex **5** has an extremely narrow molecular weight distribution (M_w/M_n 1.13; Table 1, entry 10). Moreover, polymerization with complex **5**/DMAO exhibits a virtually linear increase in M_n with polymer yield, as well as a narrow molecular weight distribution (M_w/M_n 1.09−1.17) (Figure 3), indicative of living E/NB copolymerization. This is a rare example of high-efficiency room-temperature living E/NB copolymerization.[5]

We previously reported that, in addition to a fluorinated Ti-FI catalyst, a nonfluorinated version can also exhibit some characteristics of a living E polymerization (e.g., complex **1**, 25 °C, 1-min polymerization; M_w/M_n 1.12, M_w 58 000) though under limited conditions.[7b,7c,10c,14] In fact, E polymerization complex **5**/DMAO furnished PE with a very narrow molecular weight distribution (M_w/M_n 1.18, M_w 6400) after 10-s polymerization, although the value of M_w/M_n was broadened for 5-min polymerization (M_w/M_n 2.85, M_w 436 000) (cf. complex **6**: 10-s polymerization, M_w/M_n 1.85, M_w 14 000). Considering that an NB-last-inserted species is chain-transfer-wise stable due to the difficulty in β-H transfers, the same characteristics of living E polymerization (which renders an E-last-inserted species chain-transfer-wise stable) are responsible for the living E/NB copolymerization behavior displayed by complex **5**/DMAO.[5d] Additionally, an E-last-inserted species is probably stabilized against chain transfers by the coordination of NB to the highly electrophilic Ti center, which also contributes to the living copolymerization. Future work will center on a detailed mechanistic investigation and the preparation of E- and NB-based polymers with new architectures.

In summary, we have demonstrated that bis(phenoxy−imine) Ti complexes (Ti-FI catalysts) incorporating the phenyl group *ortho* to the phenoxy-O, with DMAO activation, displayed significantly enhanced NB incorporation, together with high catalytic activity. These Ti-FI catalysts can form (monodisperse) alternating copolymers. The results described herein stand as further evidence that the highly electrophilic nature of the catalysts is of central importance for achieving efficient NB coenchainment.[5d]

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Supporting Information Available: Text giving general procedures and materials and polymerization results, and DFT calculations, tables of polymerization data and figures showing ^{13}C NMR spectra for E/NB copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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