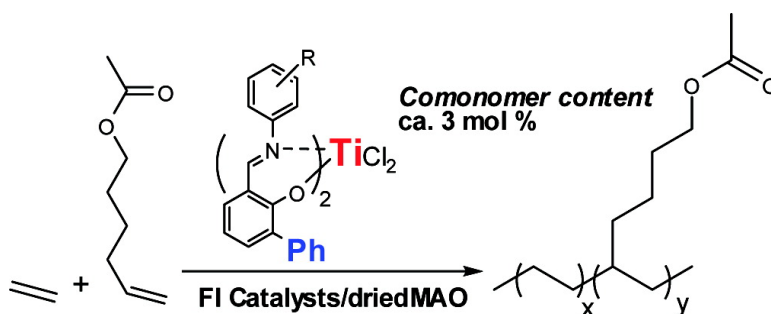## Communication

Ethylene/Polar Monomer Copolymerization Behavior of Bis(phenoxy–imine)Ti Complexes: Formation of Polar Monomer Copolymers

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Ethylene/Polar Monomer Copolymerization Behavior of Bis(phenoxy–imine)Ti Complexes: Formation of Polar Monomer Copolymers

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For some years now, academic and industrial scientists have been hard at work trying to discover molecular catalysts that allow for the copolymerization of olefinic hydrocarbon and polar monomers.[1] This is because polyolefins having polar functional groups are believed to possess not only modified surface properties such as dyeability, adhesion, and wettability, but also unique bulk properties.

For the copolymerization of olefinic hydrocarbon and polar monomers, late transition metal catalysts have been at the forefront of catalyst development.[2,3] Conversely, although early transition metal catalysts represented by metallocene catalysts have offered remarkable opportunities for the synthesis of novel olefin-based materials,[4] they are normally regarded as unpromising for such a copolymerization. This is because early transition metal catalysts are typically oxophilic and thus are deactivated by the presence of polar monomers in a polymerization medium. Therefore, these early transition metal catalysts have limited applications and require reaction modifications such as masking the functionality as an innocuous species and/or precomplexation of functional groups by stoichiometric amounts of Lewis acidic species.[1a,5]

We have found that bis(phenoxy–imine) group 4 transition metal complexes (now known as FI catalysts) with appropriate cocatalysts exhibit unique and versatile polymerization catalysis, including highly isospecific and syndiospecific polymerizations of both propylene and styrene.[6,7] As part of our investigations into FI catalysis, we studied ethylene/polar monomer copolymerization using FI catalysts, resulting in the discovery of Ti-FI catalysts capable of promoting the copolymerization of ethylene and 5-hexene-1-yl-acetate. We therefore describe ethylene/5-hexene-1-yl-acetate copolymerization behavior of a series of Ti-FI catalysts in this Communication.
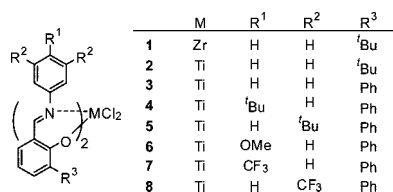

	M	R^1	R^2	R^3
1	Zr	H	H	^{t}Bu
2	Ti	H	H	^{t}Bu
3	Ti	H	H	Ph
4	Ti	^{t}Bu	H	Ph
5	Ti	H	^{t}Bu	Ph
6	Ti	OMe	H	Ph
7	Ti	CF$_3$	H	Ph
8	Ti	H	CF$_3$	Ph

Figure 1. FI catalysts employed in this study.

Shown in Figure 1 are bis(phenoxy–imine) Zr and Ti complexes (Zr- and Ti-FI catalysts) **1**−**8** utilized in this study, which were synthesized either according to published procedures or in a similar manner.[8] An X-ray diffraction study has revealed that although complex **3** (R^3 = Ph) adopts the same configuration (*trans*-O, *cis*-N, and *cis*-Cl arrangement) as complex **2** (R^3 = *tert*-Bu), it possesses a sterically more encumbered environment around the Cl-bound sites (potential polymerization sites) in the

solid state (distance between the Cl and its nearest C in the *tert*-Bu or Ph group, complex **2**; 3.97 Å, complex **3**; 3.76 Å).[6]
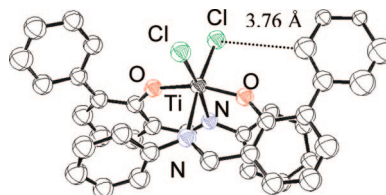

Figure 2. Molecular structure of complex **3**.

Common FI and metallocene catalysts; namely, complexes **1** and **2**, Cp$_2$MCl$_2$ (M = Zr, Ti) and Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$ (CGC) were investigated for their potential as ethylene/5-hexene-1-yl-acetate copolymerization catalysts using dried MAO (DMAO) as a cocatalyst. The results demonstrated that complex **1**, Cp$_2$MCl$_2$ (M = Zr, Ti) and CGC displayed practically no reactivity under the given conditions, generating neither polymeric nor oligomeric materials probably because of the deactivation caused by the coordination of the carbonyl moiety of the polar monomer. To our surprise, however, bis(phenoxy–imine)Ti complex **2** afforded a high molecular weight product that contains 0.13 mol % of 5-hexene-1-yl-acetate (Table 1, entry 1), which may suggest the considerable potential of Ti-FI catalysts for polar monomer copolymerization.

To obtain further information about the catalytic properties of Ti-FI catalysts for this copolymerization, we studied complexes **3**−**8**, which displayed higher ethylene polymerization activities than complex **2** (see Supporting Information). Copolymerization results are compiled in Table 1.

Complexes **3**−**7** produced copolymers with enhanced polar monomer contents (0.50−0.90 mol %). These results show that the phenyl group *ortho* to the phenoxy-O induces higher polar monomer incorporation than the *tert*-Bu group. While this appears contradictory to the X-ray structures, density functional theory (DFT) calculations indicate that the phenyl group provides a sterically more open active site than the *tert*-Bu group due to its rotation to evade the steric congestion (Figure 3). Increasing the amount of charged 5-hexene-1-yl-acetate resulted in the higher incorporation of this monomer (entries 8−11, ca. 2 mol %). Significantly, complexes **3** and **4** produced copolymers even in the presence of an excess amount of 5-hexene-1-yl-acetate to DMAO (entries 13, 14).

The copolymers formed with complexes **3**−**7** possess narrow molecular weight distributions (M_w/M_n, 1.6−2.4), as expected for a polymer generated from a chemically homogeneous catalyst. GPC-IR together with ^{13}C NMR analysis of the copolymer obtained with complex **3** (entry 8) showed a narrow comonomer distribution and the randomly distributed nature of the comonomer (Figure 4). These results represent the first examples of group 4 metal catalysts that

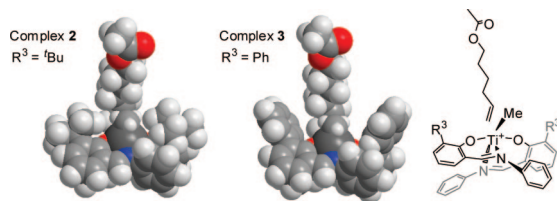exhibit high performance for the copolymerization of ethylene and a polar monomer with ester functionality.

Figure 3. Calculated structures of 5-hexene-1-yl-acetate-coordinated cationic methyl complexes derived from complexes **2** and **3**.

Table 1. Results of Ethylene/5-Hexene-1-yl-acetate Copolymerization with Complexes **2**–**8**[a]

entry	complex	comonomer[b] (mmol)	yield (g)	activity[c]	comonomer content[d] (mol %)	M_w[e] ($\times 10^{-3}$)	M_w/M_n[e]
1	**2**	1.00	0.287	86	0.13	497	2.1
2	**3**	1.00	1.12	337	0.81	269	2.2
3	**4**	1.00	1.14	341	0.90	273	2.2
4	**5**	1.00	1.72	515	0.74	387	2.4
5	**6**	1.00	1.17	353	0.66	252	2.2
6	**7**	1.00	0.593	178	0.50	190	2.4
7	**8**	1.00	0.093	28	—[f]	—[f]	—[f]
8	**3**	2.00	0.227	68	1.97	59	1.8
9	**4**	2.00	0.235	71	1.90	69	1.7
10	**5**	2.00	0.202	61	1.82	67	2.2
11	**6**	2.00	0.185	56	1.98	55	1.8
12	**7**	2.00	0.058	17	—[f]	—[f]	—[f]
13	**3**	5.25	0.035	11	2.45	20	1.8
14	**4**	5.25	0.051	15	3.20	23	1.6

[a] Conditions: toluene, 250 mL; complex, 20 μmol; DMAO, 5.00 mmol as Al; 25 °C, 10 min, ethylene, 0.1 MPa. [b] Charged 5-hexene-1-yl-acetate. [c] As kg of polymer/(mol of cat. h). [d] Determined by ^{1}H NMR. [e] Determined by GPC using PS calibration. [f] Not determined.
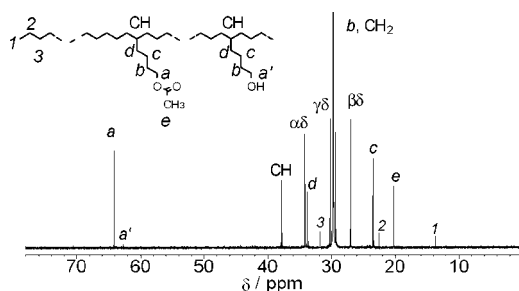

Figure 4. ^{13}C NMR spectrum for the copolymer formed with complex **3**/DMAO (entry 8).

There is no clear relationship between the product molecular weight and the nature of the substituent. Conversely, the data in Table 1 shows that the introduction of an electron-donating group (*tert*-Bu, OMe) results in a higher catalytic activity whereas the introduction of an electron-withdrawing one (CF₃) leads to a lower catalytic activity. In particular, pronounced effects were observed for complexes **5** and **8** that bear two such groups (entries 4 and 7). These results provide a clear demonstration that the electrophilic nature of the Ti center plays a crucial role in determining catalytic activity. A reasonable explanation is that a less electrophilic Ti center, generated by a more electron-donating ligand, exhibits a lower affinity to the polar functional group, giving rise to an enhanced catalytic activity.

For the purposes of having a quantitative discussion on the ligand effect on polar monomer copolymerization, we estimated the energy difference (ΔE) between ethylene-coordinated and carbonyl-coordinated cationic complexes (an indication of functional group tolerance). The carbonyl-coordinated cationic methyl complexes are more stable, and the ΔE values obtained with complexes **2**−**8** are 47.9 (**2**), 55.7 (**3**), 55.4 (**4**), 45.2 (**5**), 37.4 (**6**), 49.5 (**7**), and 60.5 kJ/mol (**8**), which are much smaller ΔE values than the ΔE values for the metallocene catalysts [104.6 (Cp₂TiCl₂), 108.8 (Cp₂ZrCl₂), 104.9 kJ/mol (CGC)]. These results indicate that Ti-FI catalysts display much higher functional group tolerance than the metallocene catalysts though both are group 4 metal catalysts, probably because of the coordination of [O⁻, N] ligands (already "poisoned"). The basic trend observed is that the introduction of an electron-donating group to the phenyl on the imine-N leads to smaller ΔE values, and *vice versa*. These calculation results are essentially consistent with the experimental data described so far, suggesting the possibility of a rational catalyst design using theoretical methods. Further research on copolymerizations using other polar monomers as well as theoretical studies is underway.

In summary, we have demonstrated that bis(phenoxy–imine) Ti complexes (Ti-FI catalysts) are potent catalysts for ethylene/5-hexene-1-yl-acetate copolymerization. The steric and electronic nature of the substitution groups of the FI ligands has a significant effect on copolymerization behavior, which can reasonably be explained by DFT calculations. The results introduced herein may open the door to polar monomer copolymerization with early transition metal catalysts.

Supporting Information Available: Synthesis of **4**−**8**, crystallographic information file (CIF) for **3**, polymerization procedures and results, GPC-IR data, DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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