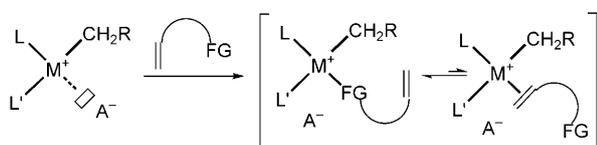


# [O<sup>-</sup>NS<sup>R</sup>]<sup>-</sup>TiCl<sub>3</sub>-Catalyzed Copolymerization of Ethylene with Functionalized Olefins\*\*

Xiao-Hong Yang, Chun-Rong Liu, Cong Wang, Xiu-Li Sun, Yang-Hui Guo, Xin-Ke Wang, Zheng Wang, Zuwei Xie, and Yong Tang\*

Much attention has been paid to the copolymerization of ethylene with polar alkenes catalyzed by transition-metal complexes, because it provides easy and low-cost access to functional polyethylenes (PEs) with unique properties.<sup>[1]</sup> Since the active species in olefin polymerization are metal cations in most cases, the polar alkene monomer will poison and deactivate the catalytic species under the polymerization conditions (Scheme 1). Two strategies, either the use of late-



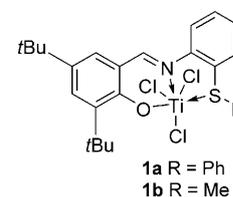
Scheme 1. Catalyst poisoned by polar alkenes. FG = functional group.

transition-metal catalysts<sup>[2]</sup> or masking the functional group of polar alkenes with Lewis acids,<sup>[3–5]</sup> have been developed as solutions to this problem. Even so, only very few catalysts exhibit high activity to afford polymer with good contents of polar comonomers. The development of an excellent catalyst to copolymerize ethylene with functional olefins in high activity and with good incorporation ratio remains a challenge.

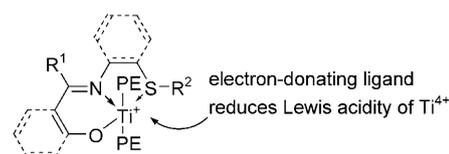
Several titanium complexes are powerful catalysts for olefin polymerization.<sup>[6]</sup> Compared with the late-transition-metal and zirconium catalysts, however, they are normally

regarded as poor catalysts for the copolymerization of ethylene with polar alkenes because of their high oxophilicity.<sup>[4]</sup> Recently, Fujita and co-workers documented that, by using an elegant bis(phenoxyimine)–titanium complex (Ti-FI) catalyst and dry methylaluminoxane (DMAO), ethylene can copolymerize with acetyl-protected hex-5-en-1-ol (hex-5-enyl acetate) with an activity of up to  $5.15 \times 10^5$  g polymer (mol Ti)<sup>-1</sup>h<sup>-1</sup> and 0.74 mol % incorporation ratio.<sup>[5d]</sup> These complexes produce copolymers with  $1.5 \times 10^4$  g polymer (mol Ti)<sup>-1</sup>h<sup>-1</sup> activity and

3.20 mol % comonomer content even in the presence of an excess amount of hex-5-enyl acetate relative to DMAO. Recently, we have developed a class of titanium complexes bearing tridentate ligands (**1a,b**), which are very active in the (co)polymerization of olefins.<sup>[7]</sup> We proposed that modification of the ligand on titanium may modulate the electronic properties of the reactive site and improve the tolerance to functional groups, thus promoting the copolymerization of ethylene with polar alkenes (Scheme 2). Herein, we report our efforts on this subject and the application of the resulting copolymer in chemical catalysis.



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Scheme 2. Strategy for improving the tolerance to polar olefin.

Using 9-decen-1-ol as a comonomer, we first tested the copolymerization behavior of titanium complex **1a**. By employing the typical strategy for an early-transition-metal catalyst, that is, to protect the hydroxy group with *i*Bu<sub>3</sub>Al, we were pleased to find that good activity was achieved ( $0.6 \times 10^6$  g copolymer (mol Ti)<sup>-1</sup>h<sup>-1</sup>atm<sup>-1</sup>) with good incorporation ratio of the alcohol (3.5 mol %) when the Al/Ti ratio was 1000 (Table 1). Catalyst **1b** gave slightly higher activity than **1a**. On the basis of these results, a less-hindered catalyst with strong electron-donating ligand is envisioned to be beneficial to the copolymerization and thus complex **2** was newly designed. The highest activity of  $1.0 \times 10^7$  g copolymer (mol Ti)<sup>-1</sup>h<sup>-1</sup>atm<sup>-1</sup> and the best incorporation ratio of the alcohol (11.2 mol %) were achieved when **2**/MMAO (Al/Ti

[\*] X.-H. Yang,<sup>[†]</sup> C.-R. Liu,<sup>[†]</sup> Dr. C. Wang, Dr. X.-L. Sun, Dr. Y.-H. Guo, X.-K. Wang, Z. Wang, Prof. Dr. Y. Tang  
 State Key Laboratory of Organometallic Chemistry  
 Shanghai Institute of Organic Chemistry  
 Chinese Academy of Sciences  
 345 Lingling Road, Shanghai 200032 (China)  
 Fax: (+86) 21-5492-5078  
 E-mail: tangy@mail.sioc.ac.cn

Prof. Dr. Z. Xie

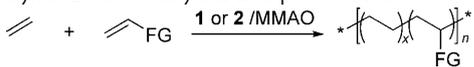
Department of Chemistry, The Chinese University of Hong Kong  
 Shatin, New Territories, Hong Kong (China)

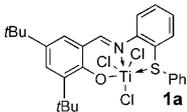
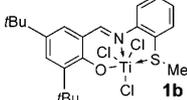
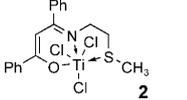
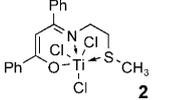
[†] These authors contributed equally to this work.

[\*\*] We are grateful for the financial support from the Natural Sciences Foundation of China (No. 20821002 and 20672131), the Major State Basic Research Development Program (Grant No. 2006CB806105), the Science and Technology Commission of Shanghai Municipality and Chinese Academy of Sciences, and NSFC/RGC of Hong Kong Joint Research Scheme (Grant No. 20710011 to Y.T. and N CUHK446/06 to Z.X.). [O<sup>-</sup>NS<sup>R</sup>]<sup>-</sup> = [(1Z,3Z)-1,3-diphenyl-3-(2-(methylthio)ethylimino)prop-1-en-1-olate].

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200903334>.

**Table 1:** Copolymerization of ethylene with polar olefins.<sup>[a]</sup>



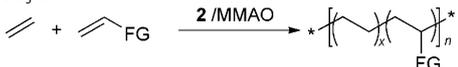
Entry	Precatalyst	FG	Act. <sup>[b]</sup>	Inc. <sup>[c]</sup> [mol %]	$M_w(10^4)$ [g mol <sup>-1</sup> ]	PDI <sup>[d]</sup>
1		(CH <sub>2</sub> ) <sub>8</sub> OH	0.6	3.5	94.0	2.9
2		(CH <sub>2</sub> ) <sub>8</sub> OH	0.7	3.4	11.5	2.2
3 <sup>[e]</sup>		(CH <sub>2</sub> ) <sub>8</sub> OH	10.1	11.2	17.8	2.2
4 <sup>[f]</sup>		(CH <sub>2</sub> ) <sub>8</sub> COOH	11.2	1.6	8.6	2.8

[a] Polymerization conditions:<sup>[8]</sup> catalyst (3.5 μmol), polar olefin (1.0 M solution in toluene pretreated with 1.2 equiv *i*Bu<sub>3</sub>Al, 20 mmol), ethylene (0.1 MPa), toluene (50 mL), 25 °C, MMAO/Ti=1000, 10 min; the incorporation ratio was determined by <sup>1</sup>H NMR spectroscopy;  $M_w$  and  $M_w/M_n$  were determined by high-temperature gel-permeation chromatography (GPC). [b] Activity, 10<sup>6</sup> g polymer (mol Ti)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>. [c] Incorporation ratio g mol<sup>-1</sup> and determined by <sup>1</sup>H NMR spectroscopy. [d] Polydispersity index:  $M_w/M_n$ . [e] 1.0 min. [f] 1.5 min and 10-undecenoic acid (1.0 M solution in toluene pretreated with 2.2 equiv *i*Bu<sub>3</sub>Al, 2 mmol). MMAO=modified methylaluminoxane;  $M_w$ =weight-average molecular weight;  $M_n$ =number-average molecular weight.

ratio 1000) was employed. The activity was 16 times higher than that when complex **1a** was used under the same conditions (Table 1). It is reported that ω-alkenoic acids, such as 10-undecenoic acid, are very poor comonomers for copolymerization and only very low incorporation ratios were observed.<sup>[3c,5b]</sup> Upon activation with MMAO, **2** is noticeably highly active in the copolymerization of ethylene with 10-undecenoic acid with an activity of 1.1 × 10<sup>7</sup> g copolymer (mol Ti)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> and 1.6 mol % incorporation ratio. The molecular weight distribution is in the range of 2.2–2.9, similar to those of PE produced by a single-site catalyst. Note that for all the copolymers obtained, the comonomers were well distributed as measured by <sup>13</sup>C NMR analyses.<sup>[8]</sup>

Noticeably, even without pretreating the comonomer with *i*Bu<sub>3</sub>Al, the copolymerization still proceeds very well upon activation with MMAO in an Al/Ti ratio of 3000:1. As shown in Table 2, catalyst **2** promoted the efficient copolymerization of ethylene with 10-undecenoic acid or 9-decen-1-ol, which afforded functional PE with high activity (up to 1.2 × 10<sup>6</sup> g copolymer (mol Ti)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>) and good incorporation ratio (up to 3.7 mol %; Table 2, entries 1 and 2), although both alcohol and acid consumed at least one equivalent of MMAO during the polymerization. 4-Penten-1-ol is also a suitable comonomer giving good activity (Table 2, entry 3). *tert*-Butyl(dec-9-enyloxy)dimethylsilane proved to be an excellent comonomer. In this case, the activity is very high with 4.2 mol % comonomer content even in the presence of an excess amount of the comonomer relative to MMAO (Table 2, entries 5 and 6). To the best of our knowledge, complex **2** offers one of the most efficient titanium catalysts

**Table 2:** Copolymerization of ethylene with polar olefins without protection with *i*Bu<sub>3</sub>Al.<sup>[a]</sup>

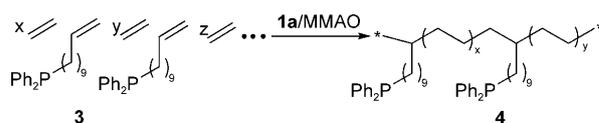


Entry	FG (mmol)	Al/Ti	Act. <sup>[b]</sup>	Inc. <sup>[c]</sup> [mol %]	$M_w(10^4)$ [g mol <sup>-1</sup> ] <sup>[d]</sup>	PDI <sup>[e]</sup>
1	(CH <sub>2</sub> ) <sub>8</sub> OH (2)	3000	1.2	3.7	8.2	1.8
2	(CH <sub>2</sub> ) <sub>8</sub> COOH (2)	3000	1.0	1.5	29.8	2.0
3	(CH <sub>2</sub> ) <sub>3</sub> OH (2)	3000	0.74	0.6	8.4	2.0
4	(CH <sub>2</sub> ) <sub>8</sub> OTBS (4)	2000	2.9	3.9	19.5	2.4
5 <sup>[f]</sup>	(CH <sub>2</sub> ) <sub>8</sub> OTBS (8)	2000	2.0	4.2	64.0	2.5 <sup>[g]</sup>
6 <sup>[f,h]</sup>	(CH <sub>2</sub> ) <sub>8</sub> OTBS (8)	2000	1.0	5.1	96.0	2.0

[a] Polymerization conditions: catalyst **2** (3.5 μmol), ethylene (0.1 MPa), toluene (50 mL), 25 °C, 10 min. [b] Activity, 10<sup>5</sup> g polymer (mol Ti)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>. [c] Incorporation ratio, g mol<sup>-1</sup> and determined by <sup>1</sup>H NMR spectroscopy. [d] Determined by high-temperature GPC. [e] Polydispersity index:  $M_w/M_n$ . [f] Toluene (80 mL). [g] Under the same conditions using ethylenebis(indenyl)zirconium dichloride as catalyst instead of **2**: activity: 0.6 × 10<sup>6</sup> g polymer (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>, incorporation ratio: 4.6 mol %;  $M_w$ : 6.9 × 10<sup>4</sup> g mol<sup>-1</sup>,  $M_w/M_n$ : 2.7. [h] 30 min. TBS = *tert*-butyldimethylsilyl.

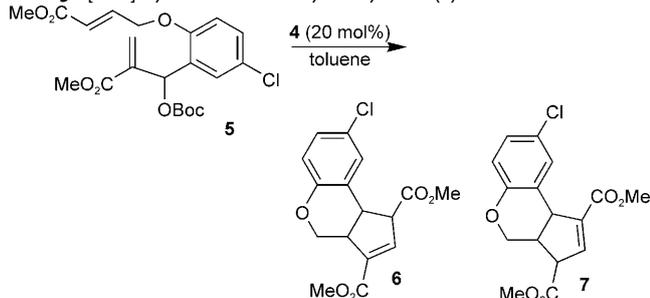
for the copolymerization of ethylene with ω-alkenol and ω-alkenoic acids.

Stimulated by the aforementioned results, we envisioned that it would be possible to zipper a catalyst on PE by copolymerization of ethylene with catalyst-containing olefin, thus providing a facile and simple method for the synthesis of PE-supported catalyst with tunable loading. This polymer might serve as a temperature-controlled, soluble, recoverable, and reusable catalyst because the solubility of the PE-supported catalyst is dependent on the temperature and comonomer content. Since phosphines have been applied as powerful organocatalysts in organic synthesis, we then tried to attach a phosphine unit to the PE backbone by employing this strategy.<sup>[9]</sup> It was found that diphenyl(undec-10-enyl)phosphine (**3**) was readily incorporated into PE in the presence of **1a**/MMAO (Scheme 3).



**Scheme 3.** Zippering phosphine on PE. Activity: 3.7 × 10<sup>5</sup> g polymer (mol Ti)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> with 3.9 mol % incorporation.

As expected, PE-supported phosphine (PE-P) **4** proved to be an excellent recoverable and reusable organocatalyst. It can catalyze a formal [3+2] cycloaddition<sup>[10]</sup> (Table 3) with a much higher selectivity than the corresponding parent phosphine **3**. When 20 mol % diphenyl(undec-10-enyl)phosphine **3** was used as catalyst, the product was obtained with a molar ratio of **6/7** = 1.6:1 since the regenerated catalyst **3** will result in isomerization.<sup>[11]</sup> To inhibit the isomerization, 20 % aqueous H<sub>2</sub>O<sub>2</sub> was added during the workup to remove the phosphine. Under the same reaction conditions, however, almost no isomerization product **6** was observed when the

**Table 3:** [3+2] Cycloaddition catalyzed by PE-P (**4**).<sup>[a]</sup>


Run	6/7 <sup>[b]</sup>	Yield [%] <sup>[c]</sup>	Run	6/7 <sup>[b]</sup>	Yield [%] <sup>[c]</sup>
1	<1:40	88	6	<1:40	85
2	<1:40	96	7	<1:40	87
3	<1:40	89	8	<1:40	87
4	<1:40	87	9	<1:40	87
5	<1:40	91	10	<1:40	86

[a] Reaction conditions: **5** (132 mg, 0.3 mmol), PE-P **4** (62 mg, 20 mol%), toluene (3.5 mL), Ti(O*i*Pr)<sub>4</sub> (20 mg, 0.07 mmol), 80 °C, 7 h. [b] Determined by <sup>1</sup>H NMR spectroscopy. [c] Yield of isolated product. Boc = *tert*-butoxycarbonyl.

corresponding PE-P **4** was employed without the use of 20% aqueous H<sub>2</sub>O<sub>2</sub>. The probable reason is that the catalyst **4** precipitated quickly at room temperature. Another advantage is that PE-P **4** can be readily recovered and reused. For instance, the reaction was carried out in a homogeneous manner at 80 °C in toluene, and catalyst **4** could be easily collected after the reaction was complete by cooling the reaction mixture to room temperature. Although phosphine-functionalized polymers have been reported as good organo-catalysts,<sup>[12]</sup> most of the recovered phosphine catalysts were found to lose activity in the first five runs.<sup>[12d,e,g,j,k]</sup> As shown in Table 3, the yield is almost maintained with excellent selectivity even after ten runs, which suggests that the zippered phosphine is a highly efficient homogeneous, recoverable, and chemically stable catalyst.

In summary, we have proved a newly designed titanium complex to be an efficient catalyst for the copolymerization of ethylene with polar olefins, such as  $\omega$ -alkenol and  $\omega$ -alkenoic acid, which offers easy access to functionalized PEs with good contents of polar comonomers and high activity. In particular, by using *tert*-butyl(dec-9-enyloxy)dimethylsilane as a comonomer, the copolymerization is still highly efficient even in the presence of an excess amount of the comonomer relative to MMAO. We have also successfully applied this method to zippering organophosphine catalyst on PE, which has proved to be an efficient and recoverable initiator for [3+2] cycloaddition. This application allows PE to be used as a cheap, readily prepared, and recoverable catalyst support. The extension of the methodology to zipper other catalysts on PE is in progress in our laboratory.

### Experimental Section

**2:** A solution of (Z)-3-(2-(methylthio)ethylamino)-1,3-diphenylprop-2-en-1-one (0.66 g, 2.2 mmol) in toluene (7 mL) was added dropwise over 15 min to a solution of TiCl<sub>4</sub> (0.51 g, 2.7 mmol) in toluene (7 mL)

at -78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After removing the solvent under reduced pressure, the brown-red solid was collected and dried in vacuo to give complex **2**. Yield: 0.85 g (85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.84–7.82 (m, 2H), 7.53–7.40 (m, 6H), 7.32–7.30 (m, 2H), 6.39 (s, 1H), 4.18–4.01 (m, 2H), 3.26 (m, 1H), 2.78 (s, 3H), 2.69 ppm (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.86, 169.89, 137.64, 132.06, 129.86, 129.38, 129.13, 128.94, 127.17, 125.90, 109.54, 56.86, 38.09, 22.40 ppm; C,H,N analysis calcd (%) for C<sub>18</sub>H<sub>18</sub>Cl<sub>3</sub>NOSTi (450.63): C 47.98, H 4.03, N 3.11; found: C 47.82, H 4.04, N 3.03.

General procedure of copolymerization (Table 2): Under 1 atm ethylene, the pure comonomer (or 1.0 M in toluene for  $\omega$ -alkenoic acid) was added dropwise to a solution of the desired amount of MMAO (1.90 M in toluene), followed by toluene (50 mL). At the desired temperature, complex **2** (3.5  $\mu$ mol, 1.0 mL in dichloromethane) was added and the polymerization was carried out for 10 min (30 min for entry 6, Table 2). The reaction was quenched with concentrated HCl in methanol (1:20, v/v) and the resulting mixture was further stirred for 2 h. The precipitated polymer was collected, washed with methanol, and dried in vacuo at 60 °C overnight.

Received: June 19, 2009

Published online: September 15, 2009

**Keywords:** alkenes · copolymerization · cycloaddition · homogeneous catalysis · titanium

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