 DOI: 10.1002/masy.200751407

Experimental and Computational Approaches on the Isospecific Role of Monoester-Type Internal Electron Donor for $TiCl_4/MgCl_2$ Ziegler-Natta Catalysts

Boping Liu,[*1] *Ruihua Cheng,*[1] *Zhen Liu,*[1] *Pengyuan Qiu,*[1] *Shiliang Zhang,*[1] *Toshiaki Taniike,*[2] *Minoru Terano,*[2] *Kunihiko Tashino,*[3] *Takashi Fujita*[3]

Summary: In this work, a combination of experimental and computational approaches on the isospecific role of monoester-type internal electron donors (ED) such as phenylpropionate (PhP), ethylheptanoate (EH), methylbenzoate (MB), ethylbenzoate (EB) for $TiCl_4$/ED/$MgCl_2$ Ziegler-Natta catalysts had been performed. The propylene polymerization results revealed that the isospecificity of catalysts increases in the following order: PhP < EH < MB < EB. The subsequent molecular modeling on the electronic properties of the donors and two kinds of cluster model catalysts: $TiCl_4$/ED/$MgCl_2$ and $TiCl_4$/ED/$(MgCl_2)_4$ based on density functional theory (DFT) method was carried out. Two kinds of ED coordination on $MgCl_2$ clusters through either =O or –O– within the monoester-type ED had been disclosed. A perfect correlation between the dipole moment of ED, the coordination bond length of =O . . . Mg, the competitive coordination from –O– with Mg ion and the isospecificity of the catalysts had been established.

Keywords: internal electron donor; molecular modeling; polypropylene (PP); Ziegler-Natta polymerization

Introduction

As the most important industrial catalyst for commercial production of polyolefins, $MgCl_2$-supported Ti-based Ziegler-Natta catalyst system nowadays is still responsible for producing tens of million tons of polyethylene (PE) and polypropylene (PP) materials.[1] For PP catalysts, electron donor (ED) compound (Lewis base) is indispensable for achieving high isospecificity as well as other important properties of the catalyst. During the last decades, the development of new ED becomes one of the key targets in designing new generation PP catalysts with high performance. Up to now, several generations of heterogeneous PP catalysts with high isospecificity, high activity and other excellent properties have been successfully developed in the industrial field for synthesis of isotactic polypropylene (PP) through successive innovation of ED compounds including monoester, alkoxysilane, diester and diether etc.[1] Whereas, the mechanism regarding the origin of isospecificity of active sites particularly the isospecific role of ED in heterogeneous Ziegler-Natta catalysis are still open for discussion even after more than 50 years of exploration.[2–9] Further experimental investigation for a complete mechanistic understanding was hindered by the complexity of the heterogeneous catalyst system. In recent decades, computational molecular modeling

[1] State Key Lab of Chemical Engineering, East China University of Science and Technology, Mei Long Road 130, Shanghai, P.C. 200237, P.R. China
Fax: (+86)-21-64253159;
E-mail: boping@ecust.edu.cn
[2] School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1, Asahidai, Nomi, Ishikawa, 923-1292, Japan
[3] R&D Section, Toho Catalyst Co., LTD., 3-3-5 Chigasaki-City, Kanagawa-Pref. 253-0041, Japan

of heterogeneous polyolefin catalysis are playing more and more important role for further development in this field.[10–19]

For modeling of $MgCl_2$–supported Ti-based Ziegler-Natta catalysts, most of the researchers constructed catalyst models comprised of 4-6 layers of $MgCl_2$ crystal with periodic boundary conditions exposing the 110 or 100 surfaces for coordination of $TiCl_4$ or $TiCl_3$ and donor compounds.[18,19] In our opinion, such models are quite different with the real image of the industrial catalysts. It is a long-standing experimental fact that the most active Ti species should be coming from the edges or corners rather than the surfaces of the crystalline substrates of the catalyst.[20] In this work, experimental approaches combined with molecular modeling investigations of the $TiCl_4$/ED/$MgCl_2$ catalyst system containing monoester-type internal ED had been carried out. One dimensional $MgCl_2$ cluster was utilized as model of the catalyst support. A good correlation between the experimental data and molecular modeling results had been achieved resulting in a better and deeper understanding on the isospecific role of monoester-type internal ED in heterogeneous Ziegler-Natta catalysis.

Experimental Part

Materials

Propylene of research grade (donated by Chisso Corp.) was used without further purification. Phenylpropionate (PhP), ethylheptanoate (EH), methylbenzoate (MB) and ethylbenzoate (EB) (purchased from Wako Pure Chemical Industries, Ltd.) were used as internal electron donor (ED) after dehydration with molecular sieves. The molecular structures of these monoester-type internal EDs used in this work are shown in Figure 1. Anhydrous MgCl2 (donated by Toho Catalyst Co., Ltd.), TiCl4 (purchased from Wako Pure Chemical Industries, Ltd.), nitrogen (purchased from Uno Sanso Co.), and TEA (donated by Tosoh Akzo Co.) were used without further purification. TEA was used as heptane solution. Heptane was purified by passing through a molecular sieves 13 X column.

Catalysts Preparation

Four internal-donor-contained $TiCl_4$/ED/$MgCl_2$ catalysts namely Cat/PhP, Cat/EH, Cat/MB and Cat/EB were prepared as follows.[34] $MgCl_2$ (36 g) and ED (7.8 mL) were placed in a 1.2 L stainless steel vibration mill pot with 55 balls (25mm in diameter) under nitrogen atmosphere and ground for 30 h at room temperature. The ground product was allowed to react with $TiCl_4$ (200 mL) in a 500 mL three-necked flask at 90 °C for 2 h with stirring under nitrogen, followed by washing with 100ml heptane for 5 times. The Ti content of the catalysts were 3.30, 1.88, 1.72 and 2.02 wt% Ti for Cat/PhP, Cat/EH, Cat/MB and Cat/EB, respectively. The catalysts were used for polymerization as heptane slurry.

Propylene Polymerization

The basic procedures for semi-batch propylene slurry polymerization are described as follows. Slurry polymerization was performed in a heptane solution (200 ml) with TEA (Al/Ti molar ratio 30) as the co-catalyst. The polymerization temperature was 30 °C. Calculated amount of TEA was added to the propylene-saturated heptane solution containing ca. 0.02mmol of each catalyst. Propylene was continuously supplied to maintain the atmospheric

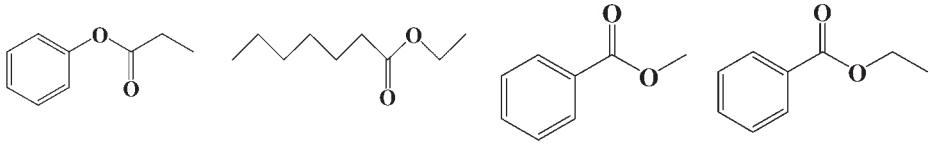

Figure 1.
The molecular structures of various monoester-type internal electron donors: Phenylpropionate(PhP), Ethylheptanoate(EH), Methylbenzoate (MB), Ethylbenzoate(EB).

pressure in the reactor. After the 10, 20 and 60 min of polymerization using each catalyst, the reaction mixture was quenched with ethanol containing 20 vol% of concentrated HCl, then the obtained polymer was washed with a large amount of ethanol and dried in vacuum at 60 °C for 6 hours. The isotacticity of the PPs in terms of mmmm% was determined by ^{13}C NMR spectra (Varian Gemini 300 spectrometer) with diluted solutions in 1,1,2,2-tetrachoroethane-d_2 at 140 °C for internal lock and the central peak of 1,1,2,2-tetrachoroethane-$d2$ (74.3 ppm) was used as an internal reference.

Computational Molecular Modeling

The computational molecular modeling on the electronic and structural properties of the electron donors (EDs) and two kinds of cluster model catalysts: $TiCl_4/ED/MgCl_2$ and $TiCl_4/ED/(MgCl_2)_4$ based on density functional theory (DFT) method (B3LYP, basis set 6-31G*, spin multiplicity: singlet for Ti(IV)) was carried out using SPARTAN'04 for PC Windows developed by Wavefunction, Inc.[15] Two kinds of ED coordination on $MgCl_2$ clusters through either =O or –O– within the monoester-type ED had been considered. The dipole moment and electrostatic charges of each internal electron donor, coordination energy of donor on $MgCl_2$ clusters and coordination bond length of O . . . Mg, etc., were obtained, and subsequent correlation with the isospecificity of catalysts was carried out in order to elucidate the isospecific role of monoester-type internal electron donor for $TiCl_4/MgCl_2$ Ziegler-Natta catalysts.

Results and Discussion

The propylene polymerization results using the four $TiCl_4/ED/MgCl_2$ catalysts namely Cat/PhP, Cat/EH, Cat/MB and Cat/EB, which contain different monoester-type internal ED, are shown in Figure 2. The polymerization activity was found to be increasing in the following order: Cat/PhP < Cat/MB < Cat/EH < Cat/EB. While, the isotacticity of PPs made from the catalysts increases in the following order: Cat/PhP < Cat/EH < Cat/MB < Cat/EB.

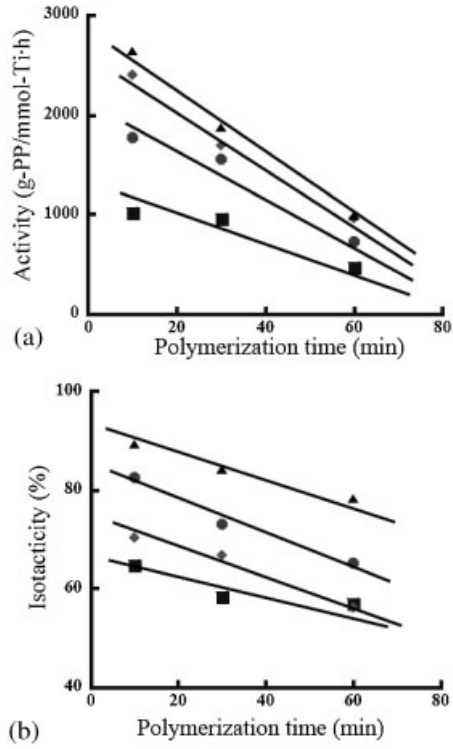

Figure 2.
The dependence of propylene polymerization activity (a) and isotacticity (mmmm% value measured by ^{13}C-NMR) of polypropylene (b) on polymerization time for $TiCl_4/MgCl_2$ catalysts with different internal ED: Cat/PhP: ■, Cat/EH: ◆, Cat/MB: ●, Cat/EB: ▲.

As a matter of fact, for both activity and isospecificity, Cat/EB is always the best catalyst with the best performance, which is consistent with the long-standing industrial evidence that EB is the best internal ED compared with any other monoester-type ED compounds for $TiCl_4/ED/MgCl_2$ catalysts. For all the four catalysts, the isospecificity of the catalyst decreased with the increase of polymerization time due to the gradual extraction of internal ED from $MgCl_2$ surface by Al-alkyl cocatalyst. The coordination strength of ED on $MgCl_2$ surface should be in the following order: PhP < EH < MB < EB judging from the

experimental results shown in Figure 2(b). The subsequent computational molecular modeling of this catalyst system will focus on the isospecific role of these monoester-type internal ED through correlation between experimental data and computational results.

Based on DFT calculations, the equilibrium geometries of various monoester-type internal electron donors: PhP, EH, MB and EB, are shown in Figure 3. The dipole moment and electrostatic charge (ESC) of oxygen atoms of the EDs were also calculated and the results were shown in Table 1. It is very interesting to find that the dipole moment of the EDs is increasing in the following order: PhP = EH < MB < EB, showing a wonderful correlation with the isospecificity of the catalysts prepared from these internal EDs. The dipole moment will decrease when the alkyl group of the monoester-type ED changes from ethyl (for EB) into propyl (1.78 debye for propyl benzoate). The results indicate that the highest dipole moment for EB might be one of the key factors for the highest isospecificity of the $TiCl_4$/EB/$MgCl_2$ within all the catalysts containing monoester-type internal ED. The ESC difference (△ESC) between the two oxygen atoms of the ED is also important factor. Higher △ESC value for MB and EB would favor the attractive Coulomb interaction between the =O and Mg ion. That is to say, the competitive coordination with Mg ion between the carbonyl oxygen (=O) and ether oxygen (–O–) must be also considered. According to further DFT calculations, the △ESC between =O and –O– of the propyl benzoate is 0.071 showing a significant decrease compared with EB and MB.

The formation of $MgCl_2$ one-dimensional (1-D) clusters was calculated by DFT method. The equilibrium geometries of 1-D $MgCl_2$ clusters: Monomer, Dimer; Trimer; Tetramer, were shown in Figure 4. The energy deceases for the formation of the Dimer; Trimer; and Tetramer from monomer are 38.04, 77.55 and 117.10kcal/mol, respectively. For a comparison, two kinds of molecular models namely $TiCl_4$/ED/$MgCl_2$ and $TiCl_4$/ED/$(MgCl_2)_4$ were constructed by DFT through subsequent coordination of $TiCl_4$ and ED on $MgCl_2$ monomer and tetramer, respectively.

Figure 5 shows the molecular model $TiCl_4$/ED/$MgCl_2$ formed by subsequent coordination of $TiCl_4$ and EB on $MgCl_2$ monomer through either the =O or the –O–. The coordination energy (CE) and coordination bond length (CBL) for catalyst models containing different internal donors: $TiCl_4$/PhP/$MgCl_2$; $TiCl_4$/EH/$MgCl_2$; $TiCl_4$/MB/$MgCl_2$; $TiCl_4$/EB/$MgCl_2$, are shown in Table 2. EB shows the highest CE and the shortest CBL for binding the carbonyl =O with Mg ion indicating the strongest binding ED on $MgCl_2$ support is the key factor in determination of the isospecific role of the monoester-type internal ED. As expected, the ether oxygen atom (–O–) of the ED do show competitive coordination behavior on the Mg ion with the carbonyl oxygen atom (=O) creating important effect on the isospecific role of the monoester-type internal ED. As shown in Table 2, generally, EB and MB show much higher □CE and □CBL values indicative of much weaker competitive coordination from their ether oxygen –O– compared with EH and PhP.

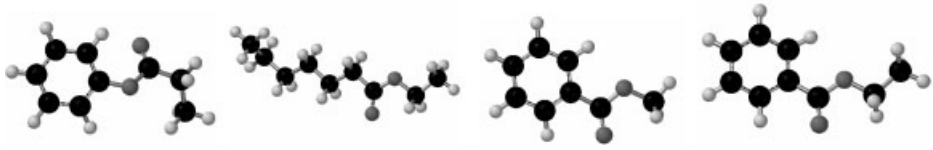

Figure 3.
The equilibrium geometries of various monoester-type internal electron donors as shown in Figure 1: PhP, EH, MB and EB.

Table 1.
Correlation of electronic properties of internal donors with tacticities of PPs produced by catalysts containing corresponding donors.

Internal Donor	Dipole Moment (Debye)	Electrostatic Charge (ESC) of O atoms within internal donor			Average Tacticity of PPs[a)]	Tactcity of PP[b)]
		=O	–O–	△ESC		
PhP	1.72	−0.480	−0.427	0.053	59.0%	55.0%
EH	1.72	−0.560	−0.443	0.117	63.3%	55.0%
MB	1.87	−0.498	−0.280	0.218	73.7%	65.0%
EB	1.99	−0.503	−0.337	0.166	83.7%	79.0%

[a)] Average Tacticity of PPs is the average isotacticity of three PPs obtained from 10, 30 and 60 min of polymerization, respectively, with the real catalysts as shown in Figure 2(b).
[b)] Tacticity of PP is the isotacticity of PP obtained from 60 min of polymerization with the real catalysts as shown in Figure 2(b).
(→ indicates increasing).

Figure 6 shows the molecular model $TiCl_4/ED/(MgCl_2)_4$ formed by subsequent coordination of $TiCl_4$ and EB on $MgCl_2$ monomer through either the =O or the –O–. It was found that the $TiCl_4$ and ED tend to preferentially coordinate at the end of the 1-D $(MgCl_2)_4$ cluster. The coordination energy (CE) and coordination bond length (CBL) for catalyst models containing different internal donors: $TiCl_4/PhP/(MgCl_2)_4$; $TiCl_4/EH/(MgCl_2)_4$; $TiCl_4/MB/(MgCl_2)_4$ and $TiCl_4/EB/(MgCl_2)_4$, are shown in Table 3. Similar to the $TiCl_4/ED/MgCl_2$ model catalyst, EB shows the highest CE and the shortest CBL for binding the carbonyl =O with Mg ion indicating the strongest binding ED on $MgCl_2$ support is the key factor in determination of the isospecific role of the monoester-type internal ED. The ether oxygen atom (–O–) of the ED also show competitive coordination behavior on the Mg ion with the carbonyl oxygen atom (=O) creating important effect on the isospecific role of the monoester-type internal ED. As shown in Table 3, in general, EB and MB

Figure 4.
Equilibrium geometries of 1-D-$MgCl_2$ clusters: Monomer, Dimer; Trimer; Tetramer.

Figure 5.
Coordination of $TiCl_4$ and subsequent coordination of internal electron donor EB through either =O or –O– on the $MgCl_2$ monomer.

Table 2.
Coordination energy and coordination bond length for catalyst models containing different internal donors: $TiCl_4/PhP/MgCl_2$; $TiCl_4/EH/MgCl_2$; $TiCl_4/MB/MgCl_2$; $TiCl_4/EB/MgCl_2$.

Catalyst Models	Coordination Energy (CE) (kcal/mol)			Coordination Bond Length (CBL) (Å)		
	=O . . . Mg	–O– . . . Mg	CE	=O . . . Mg	–O– . . . Mg	CBL
$TiCl_4/PhP/MgCl_2$	30.57	19.64	10.93	2.001	2.099	0.098
$TiCl_4/EH/MgCl_2$	31.19	19.61	11.58	1.985	2.100	0.115
$TiCl_4/MB/MgCl_2$	31.06	16.74	14.32	1.980	2.114	0.134
$TiCl_4/EB/MgCl_2$	31.45	17.35	14.10	1.979	2.101	0.122

(↓ indicates decreasing).

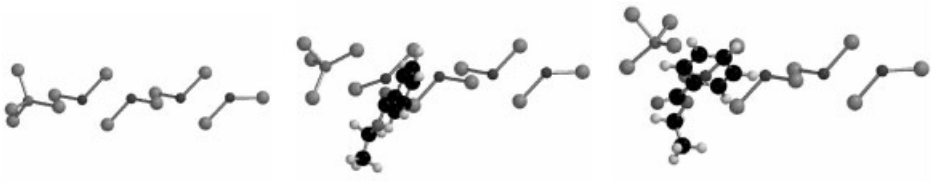

Figure 6.
Coordination of $TiCl_4$ and subsequent coordination of internal electron donor EB through either =O or –O– on the $(MgCl_2)_4$ tetramer.

show much higher CE and CBL values indicative of much weaker competitive coordination from their ether oxygen –O– compared with EH and PhP. Compared with the previous model $TiCl_4/ED/MgCl_2$, $TiCl_4/ED/(MgCl_2)_4$ shows much shorter CBL of =O . . . Mg, much higher CE and CBL values indicating increased isospecificity on the 1-D $MgCl_2$ cluster in comparison with the $MgCl_2$ monomer. For both model catalysts constructed on $MgCl_2$ monomer and $(MgCl_2)_4$ tetramer, molecular modeling results showed that the coordination strength of monoester-type internal ED on $MgCl_2$ support surface should be in the following order: PhP < EH < MB < EB, which is consistent with the experimental fact that the extractability of the four EDs by Al-alkyl cocatalyst should be in the following order: PhP > EH > MB > EB as shown in Figure 2(b).

Conclusions

The isospecific role of monoester-type internal ED in terms of the molecular structures of various monoester compounds such as PhP, EH, MB and EB for the $TiCl_4/ED/MgCl_2$ Ziegler-Natta catalysts had been studied by a combination of experimental investigations with computational molecular modeling. The propylene polymerization results using the four prepared

Table 3.
Coordination energy and coordination bond length for catalyst models containing different internal donors: $TiCl_4/PhP/(MgCl_2)_4$; $TiCl_4/EH/(MgCl_2)_4$; $TiCl_4/MB/(MgCl_2)_4$; $TiCl_4/EB/(MgCl_2)_4$.

Catalyst Models	Coordination Energy (CE) (kcal/mol)			Coordination Bond Length (CBL) (Å)		
	=O . . . Mg	–O– . . . Mg	CE	=O . . . Mg	–O– . . . Mg	CBL
$TiCl_4/PhP/(MgCl_2)_4$	24.22	9.50	14.72	1.999	2.144	0.145
$TiCl_4/EH/(MgCl_2)_4$	23.59	11.97	11.62	1.994	2.114	0.120
$TiCl_4/MB/(MgCl_2)_4$	24.50	8.84	15.66	1.978	2.154	0.176
$TiCl_4/EB/(MgCl_2)_4$	25.02	9.55	15.47	1.975	2.140	0.165

(↓ indicates decreasing).

catalysts namely Cat/PhP, Cat/EH, Cat/MB and Cat/EB revealed that the isospecificity of catalysts increases in the following order: Cat/PhP < Cat/EH < Cat/MB < Cat/EB. The subsequent molecular modeling on the four donors and two kinds of cluster model catalysts: $TiCl_4/ED/MgCl_2$ and $TiCl_4/ED/(MgCl_2)_4$ based on DFT method was carried out. The competitive coordination behavior of ED on $MgCl_2$ clusters through either =O or –O– within the monoester-type internal ED had been found. A perfect correlation between the experimental data and the molecular modeling results had been established. The key factors in determination of the isospecific role of monoester-type internal EDs for Ziegler-Natta catalysts were found to be the higher dipole moment of ED, the shorter coordination bond length of =O...Mg and the weaker competitive coordination from the –O– with Mg ion.

Acknowledgements: The authors thank Toho Catalyst Co., Ltd. for their financial support on this joint research project.

[1] E. P. Moore, Jr., "*The Rebirth of Polypropylene: Supported Catalysts*", Hanser Publishers, Munich **1998**.
[2] S. H. Kim, G. A. Somorjai, *J. Phys. Chem. B* **2002**, *106*, 1386.
[3] J. C. Chadwick, G. Morini, G. Balbontin, I. Camurati, J. J. R. Heere, I. Mingozzi, F. Testoni, *Macromol. Chem. Phys.* **2001**, *202*, 1995.
[4] G. D. Bukatov, V. A. Zakharov, *Macromol. Chem. Phys.* **2001**, *202*, 2003.
[5] V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules* **1999**, *32*, 4173.
[6] M. C. Sacchi, L. Tritto, P. Locatelli, *Prog. Polym. Sci.* **1991**, *16*, 331.
[7] B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys.* **2002**, *203*, 2412.
[8] B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys.* **2003**, *204*, 395.
[9] B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Symp.* **2004**, *213*, 7.
[10] Ø. Espelid, K. J. Børve, *J. Catal.* **2002**, *205*, 366.
[11] L. Cavallo, G. Guerra, P. Corradini, *J. Am. Chem. Soc.* **1998**, *120*, 2428.
[12] M. Seth, T. Ziegler, *Macromolecules* **2004**, *37*, 9191.
[13] M. Seth, T. Ziegler, *Macromolecules* **2003**, *36*, 6613.
[14] M. Boero, M. Parrinello, K. Terakura, *J. Am. Chem. Soc.* **2000**, *122*, 501.
[15] B. Liu, Y. Fang, M. Terano, *Mol. Simulat.* **2004**, *30*, 963.
[16] B. Liu, Y. Fang, Wei Xia, M. Terano, *Kinet. Catal.* **2006**, *47*, 234.
[17] B. Liu, W. Xia, M. Terano, *Stud. Surf. Sci. Catal.* **2006**, *161*, 129.
[18] M. Boero, M. Parrinello, H. Weiss, S. Huffer, *J. Phys. Chem. A* **2001**, *105*, 5096.
[19] T. Taniike, M. Terano, *Macromol. Rapid Commun.* **2007**, *28*, 1918.
[20] L. A. M. Rodriguez, J. A. Gabant, *J. Polym. Sci. Part-A-1* **1966**, *4*, 1971.

