J Polym Res (2014) 21:619
DOI 10.1007/s10965-014-0619-9

ORIGINAL PAPER

Ziegler-Natta catalysts with novel internal electron donors for propylene polymerization

Xiaofei Dang · Qian Li · Huayi Li · Yuan Yang · Liaoyun Zhang · Youliang Hu

Received: 24 February 2014 / Accepted: 14 November 2014 / Published online: 28 November 2014

Abstract Four new diester compounds were prepared and used as internal donors (ID) to prepare $MgCl_2$ supported titanium catalysts. Different diesters had notable influences on the porosity and the specific surface areas of the catalysts. The propylene polymerizations results showed that isopropyl groups(ID-2), cyclopentyl(ID-4) were more suitable substituents for diester compounds to replace phenyl(DIBP). The effects of different external donor (ED), Si/Ti ratio and hydrogen response on new ID precatalysts were evaluated by propylene polymerization.

Keywords Internal donor · Polypropylene · Ziegler-Natta · External donor

Introduction

Polypropylene (PP) is one of the most widely used thermoplastic resins soaring over the past few decades due to its excellent performance [1–4]. Generally, industrial manufacture of PP is derived from Ziegler-Natta polymerization [5], especially the fourth generation Ziegler-Natta catalyst, which is mainly composed of precatalyst, cocatalyst and external electron-donor (ED) compounds. Supporter, titanium component and internal electron-donor (ID) compounds together constitute the precatalyst, and the ID plays a significant role by influencing the selectivity and activity of precatalyst. In some sense the development of Ziegler-Natta catalyst is actually the exploration of ID, so great attention have been paid to the research of Ziegler-Natta catalyst, including studies of the catalytic mechanism [6, 7] and the novel electron donors designing [8, 9].

Compounds used as internal donor are mainly diesters, diethers and diketones [10]. Diamine is also used as internal donor, however the catalytic activity is not high [11]. Ch-Y Zhang has proposed phosphate as new ID and gave the PP with wide molecular distribution though the activity is not very high [12]. Nowadays the most common ID compounds in industry are diesters, especially diisobutyl phthalate (DIBP), which is a typical plasticizer known as “substance harmful to human body” [13]. Considerable efforts have been devoted to designing new ID compounds to replace DIBP, the traditional ID of the fourth generation Ziegler-Natta catalyst. Morini G proposed malonate as new ID, but the activity and isotacticity index is not very satisfied, a series of malonate structures were investigated [14–16]. Recently, novel compounds with less harm have been reported as ID of $MgCl_2$-supported catalysts, such as succinate [10, 17]. When the 2,3-substitutes are diisopropyls, the succinate contained catalyst show best catalytic performance [18, 19], and different succinate structures are investigated [20, 21]. Glutarate are also investigated as ID, and the activity and isotacticity is not very high [22–24], but when the β-substitute is isopropyl, n-propyl or methyl, the performance has been improved. Besides, diol dibenzoate is also used as internal donor with excellent catalytic performance, [25–29]. Compounding internal donor technology is developed during the past few decades [12, 30–32]. But the mechanism how the change of structure of ID compounds affect the catalysts performance is not very clear.

X. Dang · Q. Li · H. Li (✉) · Y. Yang · Y. Hu
Beijing National Laboratory for Molecular Science,
CAS Key Laboratory of Engineering Plastics, Institute of Chemistry,
Chinese Academy of Science, Beijing 100190, China
e-mail: lihuayi@iccas.ac.cn

X. Dang · L. Zhang
University of Chinese Academy of Science, Beijing 100049, China

According to our previous work, we have investigated several ID compounds in the polypropylene polymerization with Ziegler-Natta catalyst [33]. In the present work, several diester ID with different substituents shown in Fig. 1, which are expected to be less harmful to human body due to its aliphatic structure, were synthesized and used to prepare precatalysts. Besides, attention is paid to structure change effect such as introduction of steric substituents and the cycloalkyl size on the catalytic performance. Since the stereoselectivity and regioselectivity of Ziegler-Natta catalyst largely lie on the balance between the ID and ED [34, 35], the study also focuses on the performances of new ID precatalyst with different ED by propylene polymerization.

ID-1: Diisobutyl maleate; ID-2: Diisobutyl 2,3-diisopropylmaleate; ID-3: Diisobutyl cyclohexane-1,2-dicarboxylate; ID-4: Diisobutyl cyclopentane-1,2-dicarboxylate.

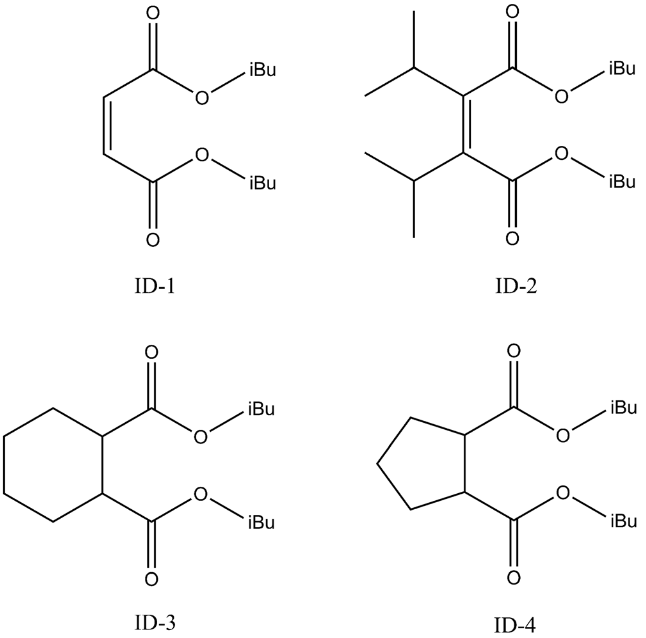


Fig. 1 Structures of the prepared internal donors

Experimental

Materials

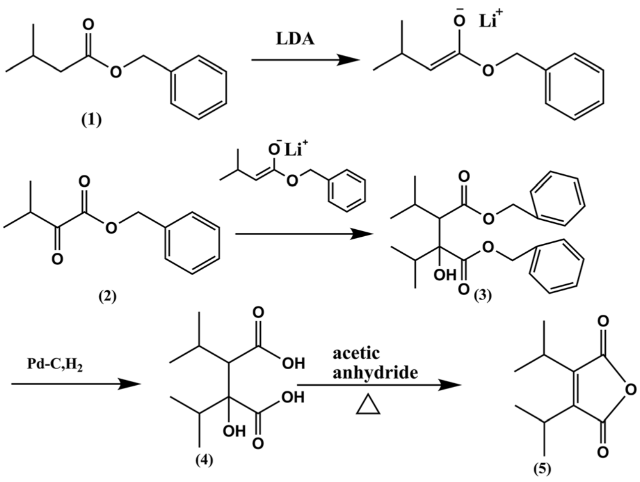
Titanium tetrachloride($TiCl_4$), diethyl oxalate, tetrahydrofuran(THF), isobutanol, lithium diisopropyl amide(LDA, 2.0 M), benzyl isovalerate, cyclohexanone, maleic anhydride, bromine, anhydrous magnesium sulfate($MgSO_4$), anhydrous magnesium dichloride($MgCl_2$) and diisobutyl phthalate(DIBP) were purchased from Aladdin Co. Ltd., and used as received. Benzyl 3-methyl-2-oxobutyrate (AR) was purchased from Beijing HiHealth Pharma. & Tech. Co. Ltd. Hexane and heptane were refluxed over sodium for 24 h to remove oxygen and moisture. Isooctanol and n-decane were commercially available as special grade and purified immediately before use by distillation from sodium under nitrogen atmosphere. Polymerization-grade propylene and triethyaluminium(TEA) were provided by Sinopec Beijing Yanshan Company.

Preparation of 2,3-diisopropyl maleic anhydride [36]

The reaction is presented in Scheme 1. LDA solution in THF (180 mL, 2 M) was cooled to −78 °C under nitrogen atmosphere, to which a solution of benzyl isovalerate (1) (57.7 g, 0.3 mol) in THF (150 mL) was added over 1.5 h, and the reaction mixture was further stirred for 1.5 h. The resulting cold solution of enolate was added into a solution of (2) (58.5 g, 0.28 mol) in THF (100 mL) which had been cooled to −78 °C. After stirring for 3 h, the reaction mixture was adjusted to pH=4 with acetic acid at room temperature. Then the reaction solvent was extracted with ethyl acetate. The organic phase was washed with 1 M hydrochloric acid, saturated aqueous solution of sodium bicarbonate and brine, respectively, then dried ($MgSO_4$), filtered and evaporated to give crude product (3) (yield 66 %) as yellow oil.

Product (3) was then dissolved in THF (50 mL), and the solution was stirred in the presence of 10 % palladium/carbon (3 g) with hydrogen bubbling at room temperature for 15 h. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. The obtained oil was added into excess acetic anhydride and stirred at 100 °C for 2.5 h. After evaporating the excess of acetic anhydride and refining by sublimation, product (5) was obtained (yield 90 %). ^{13}C NMR ($CDCl_3$) δ (ppm): 168.7, 141, 28, 20.

The product (5) reacted with isobutanol to obtain internal electron donor (ID-2). After washing and drying, the organic



Scheme 1 Preparation of 2, 3-diisopropylmaleic anhydride

phase extracted from reaction mixture thus obtained was subjected to silica gel column chromatography (petroleum ether-ethyl acetate 15:1 *v/v*) to give the product as light brown oil (yield 66 %).^{1}H NMR (CDCl$_3$) δ (ppm): 3.8 (d, 4H), 2.8 (m, 7H), 1.9 (m, 2H), 1.3 (d, 12H), 2.1 (d, 12H)

Preparation of cyclopentane-1,2-dicarboxylic acid

The reaction process is shown in Scheme 2.

Step 1: Preparation of ethyl 2-oxocyclohexanecarboxylate (8) [37]

Sodium (23 g) was added into anhydrous ethyl alcohol (300 mL) in a three-necked round bottom flask under nitrogen. After complete reaction, the mixture of cyclohexanone (103.5 mL, 1 mol) and diethyl oxalate (135.7 mL, 1 mol) was added drop wise to the flask under stirring in 15 min at 10 °C, and stirred intensely to avoid agglomeration for 6 h at room temperature. Then a mixture (300 g) of ice and sulfuric acid (1:5 in weight) was added slowly, and stirred to get a new mixture, which should now be acidic in terms of pH value. The mixture was diluted with cold water to about 4 L. The ethyl 2-ketocyclohexylglyoxalate (7) was separated as heavy oil, combined with extracts of the residues with benzene and distilled until benzene no longer distilled.

The obtained mixture was added with iron powder and quartz sand, then heated to 120 °C for 3 h to decompose compound (7). After decomposition reaction, the mixture was distilled under reduced pressure (68–70 °C, 1 mmHg) to give a colourless liquid (8) (yield 60 %).^{1}H NMR (CDCl$_3$) δ (ppm): 3.8 (s, 3H), 2.6~1.5 (m, 9H). MS (m/z): 170 (M$^+$), 142, 124, 96, 68, 55.

Step 2: Preparation of ethyl 3-bromo-2-oxocyclohexanecarboxylate (9)

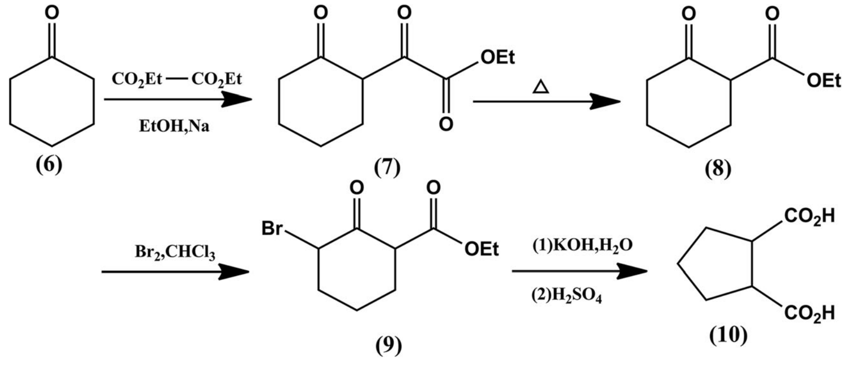
Bromine (19.2 g, 0.12 mol) was added to the solution of (8) (25.0 g, 0.12 mol) in CHCl$_3$ (75 mL) under cooling with ice in 30 min under stirring. After reaction overnight, steam was bubbled slowly to the system for 1 h, and the mixture was washed with saturated aqueous solution of sodium bicarbonate and brine, dried with MgSO$_4$. After evaporation of solvent, the residue was distilled (110~112 °C,1 mmHg) to afford yellowish liquid (9) 32.4 g (yield 86 %). ^{1}H NMR (CDCl$_3$) δ (ppm):4.70 (s, 1H), 4.25(m, 2H), 2.45~2.07 (m, 6H), 1.7(s, 1H), 1.30(t, 3H); MS (m/z): 250 (M$^+$), 205, 169, 123, 95, 67, 55.

Step 3: Preparation of cyclopentane-1,2-dicarboxylic acid (10)

(9) (30.0 g) was added under stirring to sodium hydroxide solution (100 mL, 2.5 M) under cooling with ice. After stirring for 2 h, concentrated sulfuric acid (100 mL) was added slowly, and the mixture was refluxed for 8 h. The mixture was extracted with ethyl acetate at room temperature, and the organic phase was dried with sodium sulfate, evaporated in vacuum to get reddish solid, recrystallization of which supplied white powder (10) 13.9 g (yield 73.3 %).mp:157–158 °C. IR (KBr) v (cm^{-1}):2962, 1693, 1427, 1220;^{1}H NMR (DMSO) δ (ppm):12.20 (s, 2H), 2.90 (t, 2H) 1.65~2.25 (m, 6H);MS (m/z): 168 (M$^+$), 140, 112, 95, 67.

Preparation of diesters

The preparation of the novel ID-1 to ID-4 compounds mentioned above was similar as follows. Anhydride or acid (0.05 mol) and isobutanol (30 mL) were heated to 100 °C, 0.5 mL concentrated sulfuric acid was added. The reaction mixture was refluxed and stirred for 2–3 h at 130 °C to remove water completely. After cooled to ambient temperature, the mixture was washed with distilled water, 5 % aqueous solution of sodium bicarbonate and brine respectively. After dried over MgSO$_4$, the organic phase was distilled under reduced pressure to give the product (yield 80–95 %).



Scheme 2 Preparation of 1,2-cyclopentane dicarboxylic acid

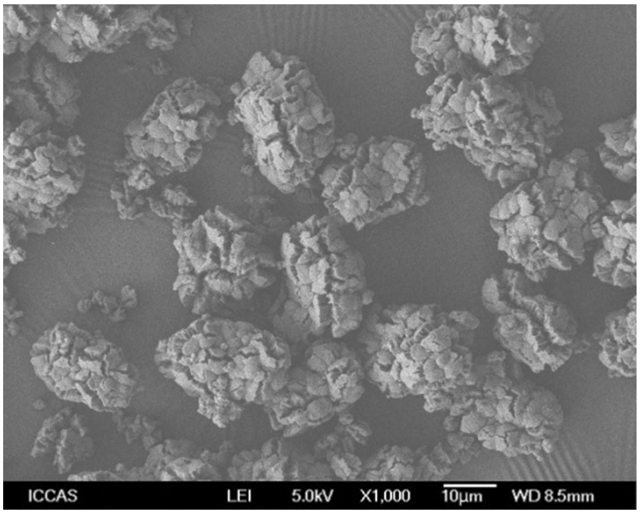


Fig. 2 Typical SEM images of the prepared catalysts

Preparation of catalyst

Anhydrous $MgCl_2$ (4.94 g), isooctanol (18.9 mL) and n-decane (30 mL) were added to a dried three-necked round bottom flask fully replaced with high-purity nitrogen. The mixture was heated to 130 °C under stirring for 2 h. A solution of tetrabutyl titanate and ID compound in toluene was added, and stirred 1 h to give a uniform and clear mixture.

The mixture was added to cold $TiCl_4$ (200 mL) of −20 °C in a five-necked reactor equipped with a mechanistic stirring bar, and heated slowly to 110 °C in 4 h. After 2 h' reaction, the $TiCl_4$ was filtered and replaced with fresh $TiCl_4$, the reaction continued for another 2 h. The final mixture was washed with hot hexane for five times, dried and restored under inert argon atmosphere.

Measurement

The particle morphology of the catalyst was determined using a JEOL scanning electron microscope (JSM-6700 F). The porosity and specific surface were performed by a fully automatic surface area and porosity tester (TriStar II 3020), manufactured by US Micromeritics Company, using nitrogen as absorbent cooled with liquid nitrogen. The X-ray diffraction (XRD) analysis was performed on X'Pert Pro which was manufactured by PANalytical from Dutch, using Co $K_{\alpha}(\lambda=0.1790$ nm) at a rate of 0.25 °/s.

The ID content was determined on gas chromatograph (clarus 580), manufactured by PE in the US. The Ti content was performed using a spectrophotometer (721), which was manufactured by Jinghua Instruments in Shanghai.

The molecular weight and molecular weight distribution were performed by the gel permeation chromatography (PL-GPC 220) manufactured by Agilent, using 1,2,4-trichlorobenzene as the eluent, and the measurement was performed at 150 °C with a rate of 1 mL/min.

Melting point (T_m), crystallizing point (T_c) and the heat of phase transition were performed using a differential scanning calorimeter (PerkinElmer, Diamond). The temperature ranged from 50 to 200 °C at a rate of 10 °C /min, and the T_m and T_c came from the second heating curve.

The isotacticity index of PP was determined by measuring the amount of boiling heptane insoluble fraction percent in the polymer.

Polymerization

Slurry polymerization was carried out under atmospheric pressure: hexane (100 mL), co-catalyst(TEA) and ED were added to a dried three-necked round bottom flask fully replaced with high-purity nitrogen. Propylene gas was added to the reactor continuously for 1 h. Then the reaction was quenched with acidified alcohol (10 % in vol), filtered, washed with alcohol, dried in vacuo for 12 h to give white polypropylene.

Bulk polymerization: the ED (2 mL, 0.16 M), co-catalyst (TEA, 12 mL, 0.88 M) and precatalyst (20 mg) were added to a 5 L tank reactor, After the addition of hydrogen and propylene (1.2 kg), the reactor was heated till 70 °C, and the polymerization time was 1 h.

Table 1 Effects of the different internal donors on the component and pore structures of the catalysts

Catalyst	Internal donor	Ti content (wt %)	Diester content (wt %)	Surface area (cm^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CAT-1	ID-1	2.8	1.2	334	0.479	5.7
CAT-2	ID-2	5.0	1.5	213	0.206	3.9
CAT-3	ID-3	4.0	2.9	351	0.249	2.8
CAT-4	ID-4	2.8	3.0	313	0.346	4.4
CAT-5	DIBP	2.9	8.7	250	0.285	4.9

Table 2 Effects of the different internal donors on the performance in propylene bulk polymerization

Catalyst	Activity (KgPP/gcat.)	Isotactic index (wt %)	$M_w{}^a$ (10^4)	M_w/M_n
CAT-1	5.6	83.5	14.1	5.1
CAT-2	23.5	97.1	18.2	6.0
CAT-3	30.0	96.8	15.5	4.7
CAT-4	20.0	95.5	14.6	5.0
CAT-5	22.5	96.4	20.0	4.0

Polymerization conditions: 20 mg catalyst, 1200 g propylene, 70 °C, Al/Ti=1000, External donor CMMS, Si/Ti=10, H_2 180 mmol, polymerization time 1 h

[a] Determined by GPC with polystyrene as a standard

Table 4 Effects of the Si/Ti ratio on the performances of the catalyst CAT-2

Si/Ti	5	10	15	20	30	40
Activity (Kg PP/g cat.)	78	100	84	50	120	80
Isotactic index (%)	96.7	97.3	97.9	96.1	95.0	95.0
T_m(°C)	161.0	160.2	160.4	160.7	161.0	160.6
ΔH_m (J/g)	100.3	96.1	94.7	93.3	94.5	96.6
T_c (°C)	115.3	114.8	114.8	114.0	113.7	113.4
ΔH_c (J/g)	104.3	102.8	92.9	92.0	101.0	103.4

Polymerization conditions: 50 mg catalyst, 0.1 MPa of propylene pressure, 45 °C, Al/Ti=100, external donor: CMMS, polymerization time 1 h, the total volume of the liquid phase was 100 mL

Results and discussion

Components and structures of the catalysts

Figure 2 shows a typical SEM image of the prepared catalysts. The morphology of the catalyst is spherical-like with a lot of cracks on it. Table 1 displays the components and pore structures of four catalysts with novel ID compounds(CAT-1 to CAT 4) and one catalyst with DIBP as ID compounds(CAT-5). As shown, the Ti contents of new catalysts are near to that of CAT-5, while the contents of ID are much lower. The surface area of CAT-1, CAT-2 and CAT 4 is higher than CAT-5. The difference indicates that the structure of synthesized ID compound has significant effect on the Ti and diester contents and pore structure of the catalysts. In traditional Ziegler-Natta catalyst with DIBP as internal donor, the Ti content usually decreases with the increasing of DIBP which could occupy more coordination sites on which Ti could have coordinated [37]. However, no regular patterns were found between the steric and electronic effects of internal donors of ID-1 to ID-5 and the components and structure parameters of the prepared catalysts. During the preparation of catalyst, the $MgCl_2$ experienced a recrystallizing process and coordination between the oxygen atom of internal donor and the metal magnesium. Since the presence of internal donor affected the decomposing process of the $MgCl_2$-donor-isooctanol and the recrystallizing process, the morphology and the structure of the support crystalline were influenced.

Polymerizing performances of the catalysts

Analyzing the polymers synthesized from the catalyst is an effective way to study the structure-performance relationship and the effect of internal donor of Ziegler-Natta catalyst on catalysis stereoselectivity and regioselectivity, on hydrogen response, and on active site distribution in the catalyst [38]. The results of the propylene polymerization with different catalysts were listed in Table 2. The isotacticity of the PP ranges from 83.5 to 97.1 %, especially CAT-2 and CAT-4 display excellent performance both in polymerization activity and isotacticity, which are close to the CAT-5 with traditional DIBP as internal donor. The molecular weight of PP derived from CAT-1 to CAT-4 are lower than CAT-5, while they show a broader molecular weight distributions. The steric effects of the five internal donors are: ID-3 > ID-2 > DIBP ~ ID-4 > ID-1, which indicates that, as internal donor, suitable steric effect of diester is appropriate for the performances of Ziegler-Natta catalyst. Therefore, two isopropyl groups(ID-2), phenyl(DIBP) and cyclopentyl(ID-4) are suitable substituents for diester compounds.

Table 3 Effects of external donor types on the performance of CAT-2 catalyst

ED type	CMMS	NPTES	TEOS	DIB	DIP	DCP
Activity (Kg PP/g cat.)	23.5	27.0	20.0	25.5	18.0	16.5
Isotactic index (%)	97.6	88.9	90.8	95.0	96.8	97.5
T_m(°C)	156.3	162.7	163.2	157.8	162.6	160.5
ΔH_m (J/g)	88.6	86.6	71.5	100.8	85.8	97.2
T_c (°C)	110.3	108.6	108.8	116.1	109.9	103.0
ΔH_c (J/g)	94.7	80.3	80.1	94.2	94.9	102.9

Polymerization conditions: 20 mg catalyst, 1200 g propylene, 70 °C, Al/Ti=1000, Si/Ti=10, H_2= 185 mmol, polymerization time 1 h

Effects of difference external donors on the CAT-2

External donor(ED) added in the polymerization also has great influence on the performance of the catalyst by balancing with ID, including catalyst activity, stereospecificity and the isotacticity sequence length distribution of PP [38–40]. Alkoxysilane is usually used as external donor, and the performance of alkoxysilane is affected by the number, size and nature of the alkoxy groups on the silicon atom [7, 41]. The effects of external donors on the performances of CAT-2 were investigated. Propylene bulk polymerizations of CAT-2 at 70 °C were carried out with different external electron donors: diisobutyldimethoxysilane (DIB), cyclohexyl- dimethoxy(methyl)silane (CMMS), dicyclopentyldimethoxysilane (DCP), triethoxy(propyl)silane (NPTES), diisopropyldimethoxysilane (DIP) and tetraethyl orthosilicate (TEOS), and the results are listed in Table 3. PP samples from NPTES and TEOS show lower isotacticity than the industry requirement (above 95 %), while DIB, DIP, DCP and CMMS show isotacticity ranging from 96 to 97.6 %. The PP activities of all external donors are above 16 kg PP /g•cat. As shown in Table 3, the thermal properties of PP samples (T_m, T_c, ΔH_m and ΔH_c) are affected by the ED structures through controlling and changing the microstructure of PP, such as isotacticity and isotacticity sequence length distribution of PP.

Effects of Si/Ti and Al/Ti ratios on the CAT-2

Besides of external donor, the Si/Ti ratio also influences the performance of the Ziegler-Natta catalyst. Table 4 shows the comparison of propylene slurry polymerization of CAT-2 with different additive contents of external donor (CMMS). With the increase of CMMS in feed, firstly the isotacticity of the PP increases to 97.9 % as the Si/Ti ratio is 15, and then decreases to 95 % as the ratio is 40. The Si/Ti ratio is observed to be an important factor affecting the melting and crystallizing enthalpies of PP.

Table 5 Effects of the ratios of Al/Ti on the performances of the CAT-2catalyst

Al/Ti	25	50	100	150	200	300
Activity (Kg PP/g cat.)	92	118	100	76	40	30
Isotactic index (%)	98.0	98.3	97.3	97.9	97.0	96.7
T_m(°C)	161.3	161.5	160.2	160.5	160.5	159.8
ΔH_m (J/g)	88.7	96.2	96.1	101.8	95.9	94.9
T_c (°C)	113.5	113.5	114.8	116.2	115.9	115.2
ΔH_c (J/g)	94.3	103.3	102.8	109.1	103.5	102.3

Polymerization conditions: 50 mg catalyst, 0.1 MPa of propylene pressure, 45 °C, Al/Ti= 100, external donor: CMMS, polymerization time 1 h, the total volume of the liquid phase was 100 mL

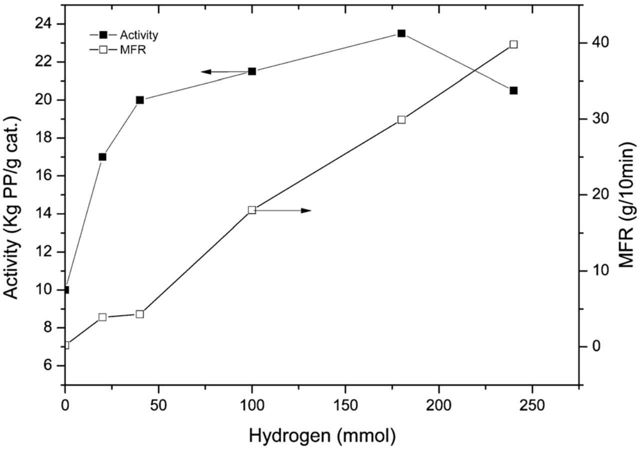


Fig. 3 Dependence of MFR on the amount of H_2

The influence of Al/Ti ratio is also investigated with CMMS as the ED (Table 5). The cocatalyst TEA initiates the catalysis polymerization, however it could remove the internal donor by alkylation and complexion reactions, making the presence of external donor necessary in polymerization. The excess TEA can replace the internal donor off the catalyst bulk and reduces the titanium to Ti^{2+} which shows no polymerizing effect [34]. It is concluded that the activity of the catalyst increases firstly and then decreases, when the Al/Ti ratio increases from 50 to 300. However, the influence of Al/Ti ratio on the isotacticity, melting temperature or crystallizing temperature of PP is not obvious.

Hydrogen response performance of CAT-2

As chain transfer agent in olefin polymerization, hydrogen is a common molecular weight regulator especially in PP manufacture. During propylene polymerization process, the present of hydrogen can accelerate the polymerizing rate because hydrogen can activate the dormant Ti centers. The hydrogen response performance in PP depends on the pairs of internal donor and external donor used in the catalyst system [7]. Figure 3 confirms that the present of hydrogen has profound

Table 6 Hydrogen response of the CAT-2

H_2 (mmol)	0	20	40	100	180	240
Activity (Kg PP/g cat.)	10.0	17.0	20.0	21.5	23.5	20.5
Isotactic index (%)	97.1	97.5	97.6	97.2	97.1	96.6
MFR (g/10 min)	0.2	3.9	4.3	18.0	29.9	39.8
M_w [a] (10^4)	30.6	20.9	23.4	18.6	15.5	15.1

Polymerization conditions: 20 mg catalyst, 1200 g propylene, 70 °C, Al/Ti=1000, Si/Ti=10, H_2=0.2 mmol, polymerization time 1 h, external donor CMMS

[a] Determined by GPC with polystyrene as a standard

Table 7 Effects of external types on the performances of CAT-4 catalyst

Si/Ti	CMMS	NPTES	TEOS	DIB	DIP	DCP
Activity (gPP/gCAT.)	82	60	56	114	120	140
Isotactic index(%)	92.4	92.7	94.8	94.3	97.0	97.7
T_m(°C)	156.9	159.7	161.6	160.3	162.6	163.9
ΔH_m(J/g)	88.6	75.1	93.1	100.8	97.0	103.1
T_c(°C)	113.6	118.2	121.2	116.1	116.8	116.3
ΔH_c(J/g)	84.2	90.7	93.8	94.2	94.9	99.7

polymerization conditions:50 mg catalyst, propylene pressure 0.1 MPa, 45 °C, Al/Ti=100, Si/Ti=10, polymerization time 1 h, the total volume of the liquid phase was 100 mL

effect on the PP molecule weight. As the hydrogen amount increases, the melt flow rate (MFR) increases apparently, while slight changes in isotacticity were observed (Table 6).

Effects of difference external donors on the CAT-4

Various external electron donors including DIB, CMMS, DCP, NPTES, DIP and TEOS were screened in propylene slurry polymerization using CAT-4. From the data in Table 7, it can be found that propylene polymerization with ID-4 as the ID shows high activity. Ideal balance in activity and isotacticity is acquired by DIP and DCP. The melting temperatures and crystallization temperatures of PP samples using DCP and DIP are also higher.

Effects of Si/Ti ratios on the CAT-4

With slurry polymerization at atmospheric pressure, the Si/Ti ratios in propylene polymerization with DIP as external donor were investigated. The results are listed in Table 8. Similar to the performance of CAT-2, the Si/Ti ratio of CAT-4 has little effect on the polymerization activity. However, the isotacticity of the PP increases to 97.9 (Si/Ti ratio 15) firstly and then decreases. The phase transition heat during melting and crystalizing process show the same tendency as CAT-2.

Table 8 Effects of the ratios of Si/Ti ratio on the performances of the CAT-4 catalyst

Si/Ti (mol/mol)	5	10	15	20	30	40
Activity (g PP/g cat.)	110	120	120	115	100	90
Isotactic index(%)	96.9	97.0	97.9	96.4	96.2	96.4
T_m(°C)	162.2	162.6	162.8	162.5	162.4	162.1
ΔH_m(J/g)	97.3	97.0	98.1	88.4	87.3	86.0
T_c(°C)	117.2	116.8	117.6	115.2	116.2	115.2
ΔH_c(J/g)	89.7	94.9	92.7	98.8	98.3	91.8

polymerization conditions:50 mg catalyst, propylene pressure 0.1 MPa, 45 °C, Al/Ti=100, external donor: DIP, polymerization time 1 h, the total volume of the liquid phase was 100 mL

Conclusion

To investigate the substituent structure effect of internal donors in PP supported catalysts, four novel diester compounds were successfully prepared and used to prepare $MgCl_2$ supported titanium catalysts. It was found that different diesters had notable influences on the porosity and the specific surface areas of the catalysts. Propylene polymerization results showed that proper substituents in the internal donors were crucial for the activities of the catalysts and the isotacticity of PP. The presence of isopropyl substituent in the ortho-position of the ester group in diester compound can improve the polymerization activity and raise the isotacticity of PP. Cyclopentanyl was better than cyclohexanyl in diester to improve the performances of the catalysts. Both the ID-2 and ID-4 had the potential to replace DIBP as the internal donors.

The effects of several external donors on the propylene polymerization using CAT-2 and CAT-4 were investigated. As for CAT-2, CMMS, DIP, DIB and DCP show higher activities and higher PP isotacticity. And for CAT-4, DIP and DCP show higher activities and higher PP isotacticity.

References

1. Kaminsky W (2008) Macromol Chem Phys 209(5):459–466
2. T. LCXGMZLH. (2005) Petrochem Technol 34:545
3. Singh G, Kaur S, Kothari AV, Naik DG, Vyas PB, Gupta VK (2009) J Appl Polym Sci 113(5):3181–3186
4. Tanase S, Katayama K, Inasawa S, Okada F, Yamaguchi Y, Konakazawa T, Junke T, Ishihara N (2008) Appl Catal A Gen 350(2):197–206
5. Wondimagegn T, Ziegler T (2012) J Phys Chem C 116(1):1027–1033
6. Kang J, Cao Y, Li H, Li J, Chen S, Yang F, Xiang M (2012) J Polym Res 19(12):1–11
7. Sacchi MC, Forlini F, Tritto I, Mendichi R, Zannoni G, Noristi L (1992) Macromolecules 25(22):5914–5918
8. Chirinos J, Fernández J, Pérez D, Rajmankina T, Parada A (2005) J Mol Catal A Chem 231(1–2):123–127
9. Vyas P, Kaur S, Patil H, Gupta V (2011) J Polym Res 18(2):235–239
10. Albizzati E, Giannini U, Morini G, Galimberti M, Barino L, Scordamaglia R (1995) Macromol Symp 89:73–89
11. Burfield DR, Tait PJT (1974) Polymer 15(2):87–96

12. Morini G, BalbonTin G, Vitale G (1999) WO Pat. 9957160
13. Barbe PC, G.; Noristi, L (1987) Adv Polym Sci 81(1)
14. Morini G (2003) EP Pat. 1395617
15. Montel Technology Company bv (1998) WO Pat. 9856830
16. Montel Technology Company bv (1998) WO Pat. 9856833
17. Barino L, Scordamaglia R (1995) Macromol Symp 89:101–111
18. Basell Technology company bv (2001) US Pat. 6313238
19. Morini G (2001) CN Pat. 1313869
20. M Ji (2008) CN Pat. 101195666
21. J-Y Dong (2008) CN Pat. 101195668
22. Montedision SPA (1982) EP Pat. 0045977
23. Mttsui Petrochemical IND (1984) EP Pat. 0125911
24. Basell (2001) CN Pat. 1313869
25. China Petroleum & Chemical Corporation Beijing Research Institute of Chemical Industry (2003) CN Pat. 1436796
26. China Petroleum & Chemical Corporation Beijing Research Institute of Chemical Industry (2003) CN Pat. 1453298
27. China Petroleum & Chemical Corporation Beijing Research Institute of Chemical Industry (2004) CN Pat. 1772740
28. China Petroleum & Chemical Corporation Beijing Research Institute of Chemical Industry (2004) CN Pat. 1542024
29. Gao MZ, Liu HT, Wang J, Li CX, Ma J, Wei GS (2004) Polymer 45(7):2175–2180
30. Morini G, BalbonTin G, Vitale G (2002) WO Pat. 0230998[P]. 2002-04-18.
31. Collina G, Fusco O, Brita D (2003) WO Pat. 03002617
32. Meesters E, New J, Guidicini A (2004) WO Pat. 2004013193
33. Yang Y, Yao J, Dang X, Li H, Hu Y (2013) Acta Polym Sin 04:511–517
34. Chadwick JC, van der Burgt FPTJ, Rastogi S, Busico V, Cipullo R, Talarico G, Heere JJR (2008) Macromolecules 37(26):9722–9727
35. Sacchi MC, Tritto I, Shan C, Mendichi R, Noristi L (1991) Macromolecules 24(26):6823–6826
36. Chikauchi K, Kurazono M, Abe T, Hiraiwa Y, Morinaka A, Kudo T, Ida M, Ken C, Mizuyo I, Takao A, Yukiko H, Akihiro M, Toshiaki K (2007) US Pat. 2008090825-A1
37. (1931) Org Synth 11.42
38. Chang H, Ren S, Dang X, Zhang L, Li H, Hu Y (2013) J Appl Polym Sci 129(3):1026–1035
39. Chang H-f, Ren S-t, Zheng T, Dang X-f, Yang Y, Zhang L-y, Li H-y (2013) Acta Polym Sin 2:199–207
40. Chang HF, Zhang Y, Ren ST, Dang XF, Zhang LY, Li HY, Hu YL (2012) Polym Chem 3(10):2909–2919
41. Proto A, Oliva L, Pellecchia C, Sivak AJ, Cullo LA (1990) Macromolecules 23(11):2904–2907