

Magnesium Chloride Supported Ziegler-Natta Catalysts Containing Succinate Internal Electron Donors for the Polymerization of Propylene

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ABSTRACT: Four of 9,10-dihydroanthracene-9,10- α,β -alkyl succinates have been synthesized and used as internal electron donors in $MgCl_2$ -supported Ziegler-Natta catalysts. The performances of the catalysts on the propylene polymerization have been investigated. The obtained polymers possess high-isotacticity and the polymerization activity is comparable with the catalysts using 9,9-bis(methoxymethyl)fluorene and diisobutyl phthalate as

internal donor. With dimethoxydiphenylsilane as external donor, the catalysts for the polymerization of propylene exhibit satisfactory activities and are sensitive toward hydrogen. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1853–1858, 2010

Key words: Ziegler-Natta polymerization; catalysts; poly(propylene)

INTRODUCTION

The large productions of polyolefins make use of heterogeneous catalysts over the world.¹ Although the catalytic polymerization of olefins has been improved with metallocenes, improvement of Ziegler-Natta catalysts have moved beyond the use of metallocene mainly, because of the discovery of the influence of electron donors. Study of the effects of internal^{2–5} and external^{6–8} donors have been carried out in academic and industrial laboratories.^{9–15} Good internal donors can produce highly active and stereospecific catalysts without any external donor.^{14,16} The widely used internal electron donors are phthalate ester and diether, such as diisobutyl phthalate (DIBP)^{17,18} and 9,9-bis(methoxymethyl)fluorene (BMMF).¹⁹

The internal donors play a remarkable role during the preparation of the solid catalyst when they stabilize small primary crystallites of $MgCl_2$ and/or influence the amount and compete with $TiCl_4$ in the

final catalyst. Additionally, the internal donor could prevent the formation of aspecific sites or transforms aspecific sites in highly stereoselective sites.²⁰ Therefore, the internal donor can strongly enhance the tacticity of the obtained polypropylene, modify the molecular mass distribution, and control the molecular mass of the produced polymers by the addition of hydrogen.

Most of the recent improvements in the heterogeneous catalyst design are related to new and better election donors. Although substituted succinates were applied as internal electron donors in Ziegler-Natta catalyst,^{21–25} the effect of the molecular structure of the internal donor on the performance of the catalyst has not been sufficiently discussed. In this article, four bulky succinates (Figs. 1–4) were selected as internal electron donors in $MgCl_2$ -supported Ti catalysts for the first time. The performances of catalysts, which include the activity of propylene polymerization, the isotactic indexes (I.I.), the molecular weights and molecular weight distributions of polypropylenes, are investigated. The effects of dimethoxydiphenylsilane (DDS) as external electron donor and hydrogen on these catalysts have also been discussed.

EXPERIMENTAL

Materials

The “activated” $MgCl_2$ supporter ($MgCl_2 \cdot 2.85C_2H_5OH$), DDS (98.5%), BMMF (99.0%), and commercial catalyst CSII (DIBP as internal donor,

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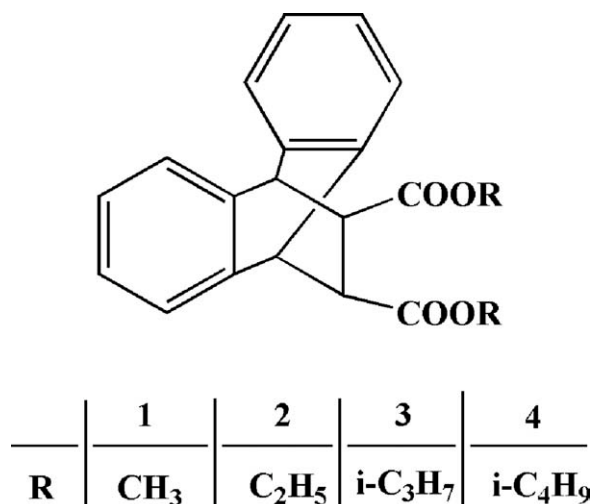


Figure 1 Structures of 9,10-dihydroanthracene-9,10- α,β -alkyl succinates.

Wt % Ti = 3.42, Wt % ID = 11.5) were kindly supplied by Yingkou Science Chemical Company (Yingkou, China). Hexane and heptane (Beijing Chemical Reagent Company, Beijing, China) were dried over molecular sieve (4Å), then refluxed for 24 h over sodium and distilled before using under nitrogen. TiCl₄ (Beijing Chemical Reagent Company), triethylaluminum (Arbemarle Company), propylene (polymerization grade, Yanshan Petrochemical Company, Beijing, China) were used without further purification.

Synthesis of internal donors

The internal electron donors were prepared according to the literature procedure.²⁶ The general syn-

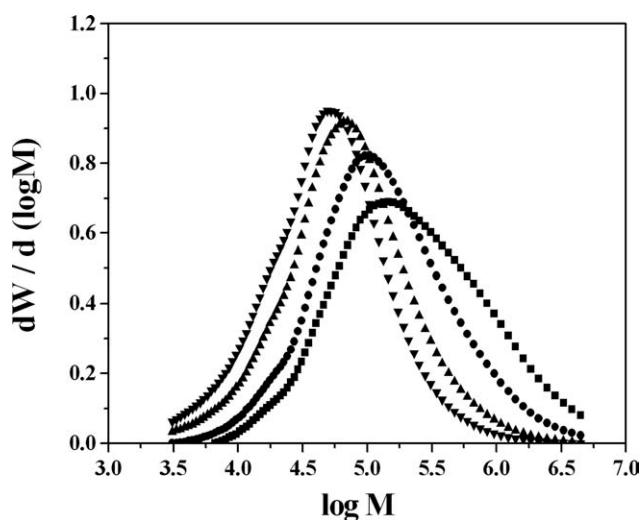


Figure 2 Results of GPC analysis of the polymers from Cat 4 with hydrogen in the polymerization reaction, (■) Cat 4, (●) Cat 4 + 1 mmol H₂, (▲) Ca 4 + 5 mmol H₂, (▼) Cat 4 + 10 mmol H₂.

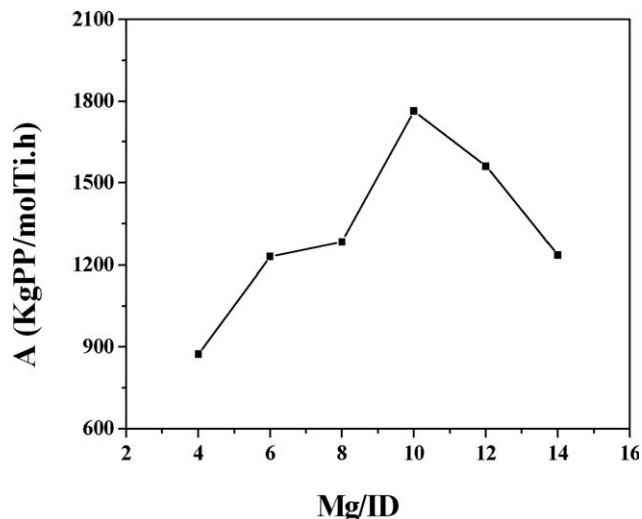


Figure 3 The effect of the amount of 4 on the activity of Cat 4.

thetic route was as follows: 9,10-dihydroanthracene-9,10- α,β -succinic anhydride and catalytic amount of p-toluenesulfonic acid in excessive alcohol were refluxed for 2 days. The reaction mixture was evaporated in vacuo to remove the alcohol and then poured into the aqueous solution of NaHCO₃. The organic phase was extracted with diethyl ether, dried over MgSO₄, and evaporated in vacuo to give 9,10-dihydroanthracene-9,10- α,β -alkyl succinate (DHA-alkyl). Four succinates with meso configuration were synthesized in this method: DHA-methyl (1), DHA-ethyl (2), DHA-isopropyl (3), DHA-isobutyl (4).

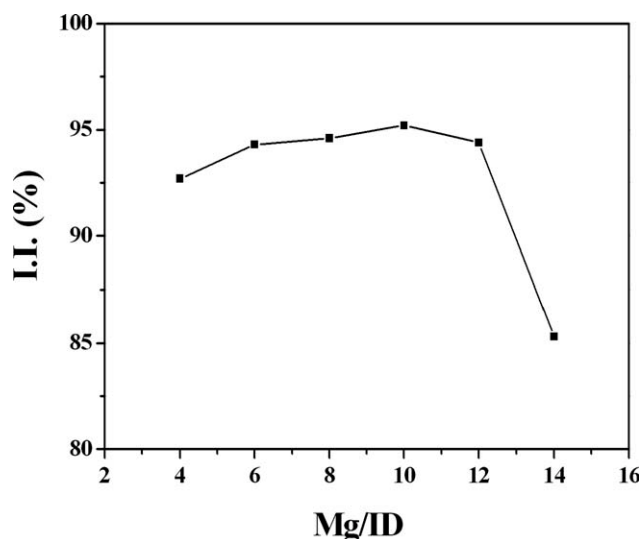


Figure 4 The effect of the amount of 4 on the isotacticity of the polymer from Cat 4.

TABLE I
Results of Propylene Polymerization Using Different Catalysts
Without External Donor

Cat. ^a	A ^a (kgPP/molTi·h)	T _m (°C)	ΔH _m (J/g)	M _n (10 ⁴)	I.I. (%)
Cat 1	64.2	152.5, 159.9	61.3	15.7	81.6
Cat 2	246.6	153.0, 160.6	66.1	10.7	75.4
Cat 3	273.4	152.5, 160.6	67.6	14.8	77.6
Cat 4	247.1	155.0, 161.1	69.1	17.7	81.7
Cat B	193.0	151.9, 158.2	89.1	13.4	88.2
CSII	155.6	154.7, 160.2	78.1	16.3	81.8

^a Polymerization conditions: catalyst: 100 mg; heptane: 100 mL; propylene pressure: 0.1 MPa; Al : Ti = 100 ([AlEt₃] = 1.8 mol/L in heptane); time: 1 h; temperature: 50°C.

Preparation of the catalyst

Under nitrogen atmosphere, a large excess of TiCl₄ was introduced into the reactor and kept at -20°C. An amount of MgCl₂·2.85C₂H₅OH was added slowly and maintained for 1 h at this temperature (Ti/Mg molar ratio = 50) with agitation. Internal donor was added, after the mixture was brought to 60°C (Mg/ID molar ratio = 4 ~ 14). The mixture was allowed to react at 120°C for 2 h with agitation. The residual solid was filtered and washed with hexane 5 times at 60°C and one time at room temperature. The final catalyst was collected in a glass vial and dried under vacuum. Five catalysts were prepared in the same process: Cat 1 (Wt % Ti = 3.82, Wt % ID1 = 9.85), Cat 2 (Wt % Ti = 2.25, Wt % ID2 = 4.06), Cat 3 (Wt % Ti = 1.91, Wt % ID3 = 13.1), Cat 4 (Wt % Ti = 2.58, Wt % ID4 = 9.61), and Cat B (BMMF as internal donor, Wt % Ti = 3.82, Wt % ID = 16.6).

Polymerization condition

At 50°C, in a 250 mL reactor previously purged with nitrogen and propylene, 100 mL anhydrous heptane, the prescribed amount of AlEt₃ and DDS (or without DDS) were introduced into the reactor under a propylene flow. When no more propylene was absorbed, a prescribed amount of catalyst was added into the heptane solution, and then the polymerization was started. Propylene pressure and temperature were kept constant during the polymerization. The polymerization was quenched after 1 h by the addition of acidified ethanol. The polymer product was collected by filtration, washed with ethanol and water, and then dried in vacuum at 60°C until the weight of the polymer was constant.

Characterization

The contents of titanium and internal donor were measured on spectrophotometer (72-1) and gas chromatograph analyzer (Techcomp GC7900) respectively. Melting points and ΔH_m of the polymers were measured by means of DSC (differential

scanning calorimetry, Perkin-Elmer DSC-7) by heating from 50 to 200°C (second fusion) at a heating rate of 10°C/min. The molecular weight M_n of the polymers were measured in decahydronaphthalene at 135 ± 0.1°C (D20kp Lauda) and converted into average viscosimetric molecular weights using the Mark-Houwink equation.²⁷ The molecular weight M_n, M_w, and polydispersity (PDI) of the polymers were obtained by Gel permeation chromatography (GPC, Waters Alliance GPC 2000) analysis of the polymers performed at 145°C using 1,2,4-trichlorobenzene as a solvent. The melt flow rate (MFR) of the polymers were measured using Haake—SWO550—0031 at 230°C. The isotacticity index (I.I.) of the polymer was determined by extracting the polymer with boiling *n*-heptane.

Result and discussion

The four catalysts containing different internal donors have been applied for propylene polymerization and compared with Cat B and the commercial catalyst CSII. The results of the slurry polymerization of propylene and the main characteristics of the resulting polymers are summarized in Table I. It can be seen that the activity of Cat 1 is only 64.2 kgPP/molTi, implying internal donor with poor steric hindrance is unfavorable to catalytic performance. Cat 2, Cat 3, and Cat 4 exhibit higher activity than Cat B and CSII, and Cat 3 shows the highest activity possibly because of a proper bulkiness, and its most amount of internal donor. In despite of satisfactory productivity, relatively low-isotacticity of the produced polypropylene were observed, accompanied by double melting points.

The role of the external donor is to poison aspecific center or generate new isospecific centers, therefore, the external donor was added during the polymerization to increase the tacticity of the polymer as depicted in Table II. As expected, the isotacticities of all the polymers are above 90%, the melting curves of the express single peaks, and most polymerization activity are reduced. The catalytic efficiency of Cat 2

TABLE II
Results of Propylene Polymerization Using Different Catalysts with
DDS as External Donor

Cat. ^a	Si :Ti ^a	A ^a (kgPP/molTi·h)	T _m (°C)	ΔH _m (J/g)	I.I. (%)
Cat 1	10	39.3	158.4	103.8	93.8
Cat 2	10	174.3	158.3	83.2	91.0
Cat 2	20	140.3	156.4	90.1	94.7
Cat 3	10	98.6	157.2	130.5	90.3
Cat 4	10	192.5	157.4	105.9	91.5
Cat 4	20	216.9	157.8	147.0	95.1
Cat B	10	92.4	158.9	118.3	98.2
CSII	10	184.8	160.1	198.4	96.8

^a Polymerization conditions: catalyst: 100 mg; heptane: 100 mL; propylene pressure: 0.1 MPa; Al : Ti = 100 ([AlEt₃] = 1.8 mol/L in heptane); time: 1 h; temperature: 50°C.

and Cat 4 are comparable with commercial catalyst CSII. The efficiency of a catalytic system was shown to be dependent on the choice of the specific pair of internal and external donor rather than on the single internal or external donor chosen. By use of the same external donor the catalytic performance are largely dependent the electron-donating ability and steric hindrance. The four catalysts perform different characteristics after adding external donor. The activity of Cat 4 with biggest bulkiness is the highest and that of Cat 1 with smallest one is the lowest.

The molecular weight and molecular weight distribution of the polymers from Cat 2 and Cat 4 were investigated and compared with those from Cat B and CSII (Table III). The molecular weight distribution of the polymers from Cat 2 and Cat 4 are broad, similar as that from CSII. While the molecular weight distribution of the polymer from Cat B is narrow. It can be interpreted that succinates with a longer spacer between the coordination O atoms adopt more variety of conformations when coordinating to Mg atoms leading to the configurational diversity of active sites, compared with diether (BMMF) with a short spacer.²⁰ The polymer formed by Cat 4 presents quite larger molecular weight than that from Cat 2. It illuminates that slight difference in molecule structures of the internal donor could cause obvious distinction of the chain transfer rate. With larger substitute group in donor 4, the catalyst Cat 4 induces lower chain transfer rate in the polymerization reaction. And the polymer from Cat 4 has larger molecular weight.

In almost all industrial process hydrogen is used as chain transfer agent for precise control of molecular weights of the polymers. There is a correlation between the hydrogen response and the isospecificity of the active sites. Propylene polymerizations with Cat 2 and Cat 4 by adding hydrogen are investigated as listed in Table IV. By addition of hydrogen to 10 mmol, the activities of two catalysts

enhance drastically, meanwhile the melt flow rate of the polymers generated by Cat 2 and Cat 4 increased from 2.64 g/10 min and 1.84 g/10 min to 96.0 g/10 min and 114.0 g/10 min, respectively. Cat 4 expresses very well regularity. Figure 2 shows that with increasing the amount of hydrogen, a clear shift to higher molar masses but also improvement in the PDI of the samples can be seen.

The effects of the content of internal donor added in the synthesis processes of the catalysts on the activities of the catalysts have been examined using internal donor 4 (Polymerization conditions: catalyst: 50 mg; heptane: 100 mL; propylene pressure: 0.35 MPa; Al : Ti = 100; Al : Si = 10; time: 1 h; temperature: 50°C). As shown in Figure 3, with elevating the molar ratio of Mg/ID, the activity of the catalyst increases. At Mg/ID = 10, it attains to the largest value. Then it reduces at higher concentration of Mg/ID molar ratio. Figure 4 depicts the effect of Mg/ID molar ratio on the isotacticity of the polymers. An obvious decrease could be observed above 10 of Mg/ID ratio. Those results are in accordance with the research regarding DMMF used as internal donor.¹⁹ According to Soga et al.²⁸ an aspecific site has two vacancies, whereas an isospecific site possesses only one vacancy. The proper introduction of

TABLE III
Results of GPC Analysis of PP polymerized Using
Different catalysts with External Donor DDS

Cat. ^a	M _n (10 ⁴)	M _w (10 ⁴)	PDI
Cat 2	2.59	29.75	11.5
Cat 4	12.7	138.0	10.9
Cat B	3.17	21.10	6.7
CSII	1.90	23.26	12.2

^a Polymerization conditions of PP: catalyst: 100 mg; heptane: 100 mL; propylene pressure: 0.1 MPa; Al : Ti = 100 ([AlEt₃] = 1.8 mol/L in heptane); Si : Ti = 10 (C_{DDS} = 0.088 mol/L); time: 1 h; temperature: 50°C.

TABLE IV
Results of Propylene Polymerization Using Cat 2 and Cat 4 with Hydrogen

Cat. ^a	H ₂ ^b (mmol)	A ^a (kgPP/molTi·h)	MFR ^c (g/10 min)	M _n ^d (10 ⁴)	M _w ^d (10 ⁴)	PDI
Cat 2	0	555.4	2.64	14.7	69.5	4.7
Cat 2	1.0	962.4	31.6	7.03	25.2	3.6
Cat 2	5.0	933.7	48.6	4.71	22.5	4.8
Cat 2	10.0	995.9	96.0	3.24	10.9	3.4
Cat 4	0	545.8	1.85	9.31	45.5	4.9
Cat 4	1.0	632.0	28.8	6.85	27.0	4.0
Cat 4	5.0	780.4	86.4	3.88	12.5	3.2
Cat 4	10.0	799.6	114.0	2.81	8.91	3.2

^a Polymerization conditions: catalyst: 50 mg; heptane: 100 mL; propylene pressure: 0.5 MPa; Al : Ti = 100 ([AlEt₃] = 1.8 mol/L in heptane); Al : Si = 10 (C_{DDS} = 0.088 mol/L); time: 1 h; temperature: 50°C.

^b Hydrogen amount added in the polymerization reaction.

^c Melt flow rate of the polymers measured at 230°C.

internal donor (Mg/ID > 10) can selectively replace one of the vacancies of the aspecific sites, the other vacancy reforms the isospecific sites, and thus the activity is improved. While the excessive amount of internal donor (Mg/ID < 10) occupies two classes of sites, leading to the lessening of the polymerization activity and isotacticity of the polypropylene.

The effects of the external donor DDS on the catalyst activities and polymer isotacticities have also been studied by using Cat 4 (Polymerization conditions: catalyst: 50 mg; heptane: 100 mL; propylene pressure: 0.35 MPa; Al : Ti = 100; time: 1 h; temperature: 50°C). The external donor usually replaced internal donor during the reaction and coordinates first with the nonisospecific Ti species, and it can take similar effect with internal donor on the catalytic polymerization behavior. Figures 5 and 6 shows that with increased amount of DDS the highest activity is reached at Si/Ti = 15, then

descended quickly. And the isotacticity of the polymers are raised with the improvement of Si/Ti.

CONCLUSIONS

The compounds 1–4 with different substituted group of succinate could be used as internal donors in MgCl₂-supported Ti catalyst. For propylene polymerization using DDS as external donor, the catalysts Cat 1–4 display moderate activities and the final polymers have high isotacticities. The polymers from Cat 2 and Cat 4 give broad molecular weight distributions. Both Cat 2 and Cat 4 are sensitive toward hydrogen. With the increase of the amount of hydrogen, the activities of the catalysts rise up, the MFR of the polymers increase, and the molecular weight of the polymers decrease. The researches on

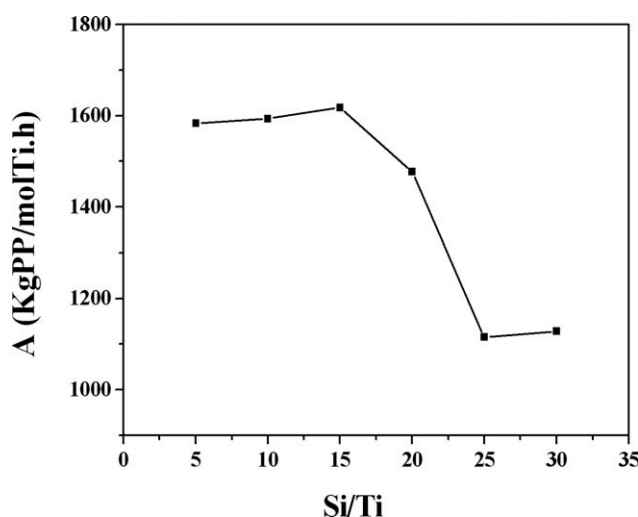


Figure 5 The effect of the external donor DDS on the activity of Cat 4.

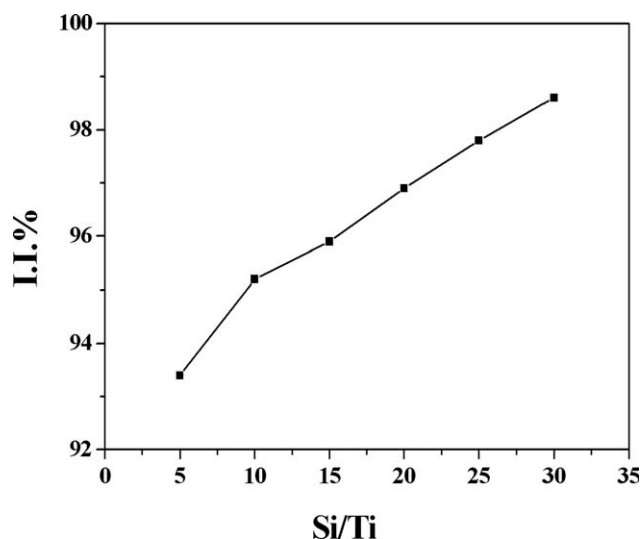


Figure 6 The effect of the external donor DDS on the isotacticity of the polymer from Cat 4.

Cat 4 indicate that the proper molar ratio of supporter and internal donor ($Mg/ID = 10$) could give high-activity of the catalyst and high-isotacticity of the polymer. At certain molar rate of DDS with the catalyst ($Si/Ti = 15$), the activity of Cat 4 is high. As the concentration of external donor DDS increases, the isotacticity of the polymer is promoted.

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