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$MgCl_2$-Supported Ziegler–Natta Catalyst Containing Dibenzoyl Sulfide Donor for Propylene Polymerization

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ABSTRACT: Polypropylene (PP) was synthesized in the presence of Ziegler–Natta catalysts composed of $MgCl_2$-$TiCl_4$-internal donor/AlR_3-external donor. Diisobutyl phthalate is a well-known internal donor in current PP production. Nevertheless, phthalates are often blamed as endocrine disruptors. The objective is to find an ecofriendly internal donor producing PP with maintaining its physical properties. When using dibenzoyl sulfide, synthesized PP shows the superiority to diisobutyl phthalate in the activity of catalyst (40 vs. 22 kg PP/g catalyst), the isotacticity of polymer (99.5 vs. 98.0 wt % of heptane insolubles), and the molecular weight distribution of PP product ($M_w/M_n = 4.8$ vs. 4). © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40743.

KEYWORDS: catalysts; polyolefins; property relations; structure

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INTRODUCTION

As Ziegler and Natta developed a method for synthesizing polyolefins, catalysts have been mainly modified to improve their activity and to enhance the degree of isotacticity of polyolefins. High isotactic and high molecular weight with broad molecular weight distribution are crucial to achieve high crystallinity and high rigidity, which is favorably applicable to extrusion process. As an early catalyst, a simple from of $MgCl_2$-$TiCl_4$/AlR_3 exhibited very low activity and poor isotacticity.[1] After Lewis base donor was introduced, even though catalyst became more complicated, the donor could control the amount of Ti absorption and active site. It was known that Ti provides active sites for polyolefin synthesis after placed by selective adsorption on its support surface and also Ti plays an important role in product characteristics.[2] Among early catalysts, $MgCl_2$-$TiCl_4$-EB/AlR_3 (EB represents ethyl benzoate as an internal donor) improved the isotacticity of polypropylene (PP) product up to 60%. In addition, the use of aromatic monoesters to both internal and external donors resulted in high isotacticity to 95%. In case that aromatic diester and silane were used as internal donor and external donor, respectively, polymer product showed high activity and high isotacticity of 97–99%.[3,4] Catalyst used diether as an internal donor could synthesize polymers bearing high isotacticity (97–99%), high activity, and narrow molecular weight distribution even in the absence of an external donor. Other studies reported the improvement in the isotacticity and the molecular weight distribution of polymer product using diethers as internal donors.[5–12] Mixed internal donor with disobutyl phthalate were reported elsewhere.[11,12] Chadwick et al. reported that high regiospecific active sites were possible to obtain high isotactic PP when diisobutyl phthalate and alkoxysilane were used as internal and external donors, respectively.[13]

Meanwhile, phthalate is frequently blamed as an endocrine disruptor. This study is motivated to replace diisobutyl phthalate by less endocrine disrupting chemicals without sacrificing PP product properties. We used various components as internal donors. Chart 1 illustrates the molecular structures of 13 components we used. Characteristics of catalysts were evaluated by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and Fourier-transform infrared spectroscopy (FTIR). Catalytic activity, isotacticity, and molecular weight distribution of PP were analyzed by gel-permeation chromatography (GPC), differential scanning calorimeter (DSC), and isotacticity index (II), respectively.

EXPERIMENTAL

Materials

Nine components of Cat-1 through Cat-9 (refer to Chart 1), propylene, hydrogen, triethylaluminium, and diisobutyl

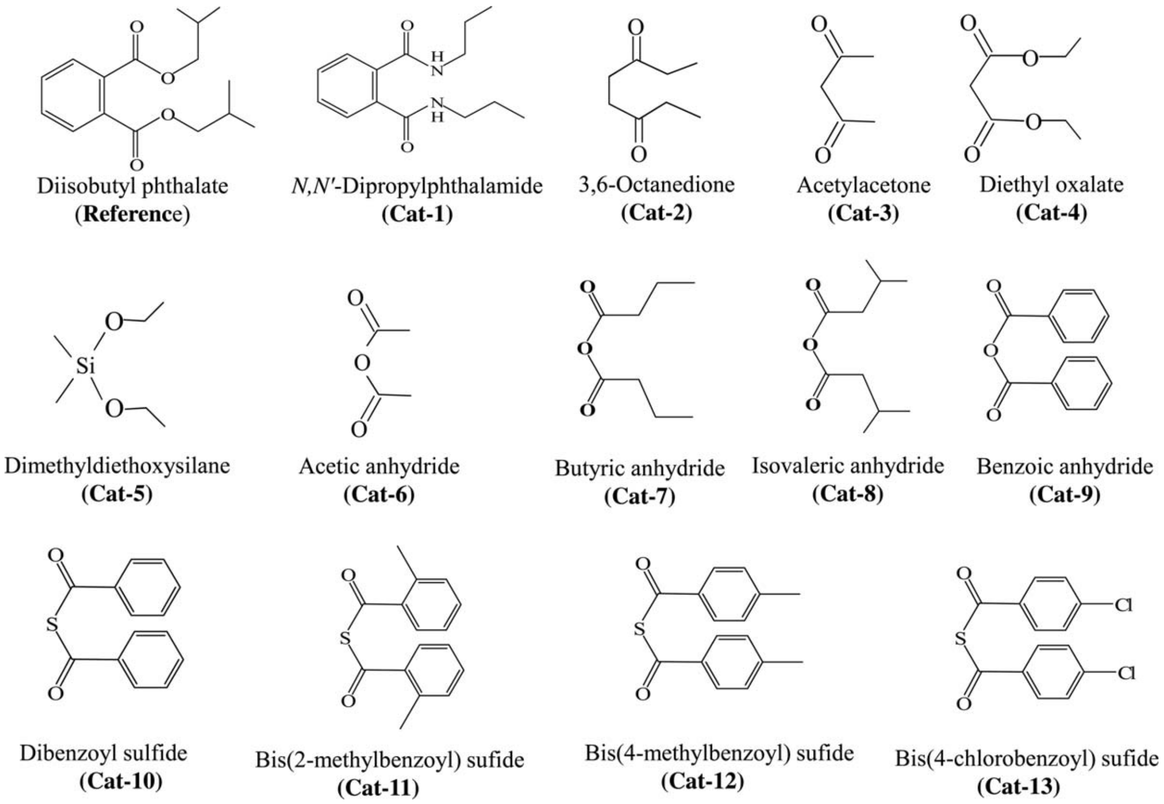

Chart 1. Chemical structures of internal donors used in this study.

phthalate were purchased from commercial suppliers as a reagent grade and used without further purification. Four components of Cat-10 through Cat-13 (Chart 1) were prepared by synthesis in laboratory. Among the synthesized components, dibenzoyl sulfide is introduced as its synthetizing procedure and characteristics thereafter.

Preparation of Dibenzoyl Sulfide

Synthesis of benzoyl sulfide was performed in a glove box under nitrogen-flowing environment. Benzoyl chloride (2.81 g, 20 mmol) was added to the LiAlHSH suspension (6.80 g, 10 mmol). The mixture was stirred at room temperature for 3 h. The organic layer in mixture was dried over sodium sulfate and evaporated. The residue was extracted with chloroform (10 mL). It was further concentrated to approximately half its volume, and cooled to −10°C. Obtained was pure white crystal. Yield: 1.82 g (75%). Mp: 103°C (dec). HRMS: Calcd. for $C_{14}H_{10}O_2S_1$ *m*/*e* 242.29, Found 243.00 Calcd.: C 69.41, H 4.16, S 13.21; Found: C 69.19, H 4.14, S 13.17; ^{1}H NMR (600.1 MHz, $CDCl_3$): δ 7.49 (t, 4H, $^3J_{HH} = 7.9$ Hz, Ar), 7.63 (t, 2H, $^3J_{HH} = 7.5$ Hz, Ar), 8.06 (d, 4H, $^3J_{HH} = 7.9$ Hz, Ar). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 128.22, 129.12, 134.55, 135.26 (Ar), 186.18 (Ar*C*O). FTIR spectrum (KBr pellet, cm^{-1}) 1720 s, 1675 s (ν_{CO}).

Preparation of Catalyst

Catalysts were prepared in a glove box under inert condition. A uniform solution was prepared after three components of anhydrous magnesium chloride (4.76 g, 50 mmol), decane (23 mL), and 2-ethyl-1-hexanol (25 mL) were mixed and reacted at 130°C for 2 h. Phthalic anhydride (1.41 g, 9.52 mmol) was dissolved to this solution and further stirred at 130°C for 1 h. After the mixture was cooled to room temperature, titanium tetrachloride (25 mL, 0.23 mol) was dropped over 1 h and placed at −20°C. The mixture was then heated to 110°C and maintained for 4 h, and internal donor (10 mmol) was injected and reacted for additional 2 h. After reaction, the supernatant was removed and the residue was washed by toluene. Precipitated solid was treated again with a mixture of toluene (200 mL) and titanium tetrachloride (25 mL, 0.23 mol) at 110°C for 2 h. After discarding supernatant, the residue was washed with toluene and hexane separately and obtained a solid catalyst. Then, we measured the particle size of catalyst using SEM and particle size analyzer. It requires careful treatment during either SEM measurement or particle size analyzer. We used anhydrous hexane as a dispersant during measuring particle size analyzer. And, we tried to minimize the breakage of catalyst particles during specimen preparation for SEM measurement.

Polymerization

After nitrogen purge, a 2-L autoclave was completely replaced by propylene gas. Then, three components of triethyl aluminum (3 mmol), dicyclopentyl-dimethoxysilane (0.18 mmol), and the catalyst (0.0033 mmol) were introduced into the autoclave. It should be noted that air-contact of catalysts was carefully

Table I. Catalytic Performance Data for Polypropylene Synthesis

Catalyst	Internal donor	CAS No.	Particle size (μm)	Activity (kg-PP/g-Cat)	Ti contents (wt %)	BD[a] (g/mL)	I.I[b] (%)
Reference	Diisobutyl phthalate	84-69-5	24	22	0.8	0.38	98.0
Cat-1	*N*,*N*′-Dipropylphthalamide	N/A	27	1.0	4.1	–	–
Cat-2	3,6-Octanedione	51513-41-8	21	9.5	3.0	–	–
Cat-3	Acetylacetone	123-54-6	27	2.0	5.7	–	–
Cat-4	Diethyl oxalate	95-92-1	24	1.5	3.7	–	–
Cat-5	Dimethyldiethoxysilane	78-62-6	22	21	1.3	–	–
Cat-6	Acetic anhydride	108-24-7	26	5.0	2.6	–	–
Cat-7	Butyric anhydride	106-31-0	25	29	1.5	0.42	98.0
Cat-8	Isovaleric anhydride	1468-39-9	22	24	0.8	0.42	98.1

Polymerization condition: 2-L reactor, $C_3H_6 = 500$ g, Ti = 3.3×10^{-3} mmol, $AlEt_3 = 3$ mmol, dicyclopentyl dimethoxysilane = 0.18 mmol, 70°C, 1 h.

[a] BD: Bulk density.

[b] Isotacticity index (weight percent of heptane insoluble fraction).

prevented through polymerization process. After 750 mL of hydrogen and 500 g of propylene were introduced into the autoclave, the temperature was raised to 70°C, and propylene was polymerized for 1 h. White powdery form of polymer product was obtained. We repeated the reaction three times and adapted the average value for polymer characterization in this experiment.

Characterization

The titanium content in the samples was determined by ICP-AES (Perkin-Elmer Optima-4300 DV). FTIR was performed to examine PP products after vacuum-dried at room temperature. FTIR spectra were recorded by Jasco FTIR 4100 spectrometer equipped with a dry nitrogen chamber and cells sealed by CaF_2 windows. All the spectra were collected at a resolution of 4 cm^{-1}. Molecular weight and molecular weight distribution of PP products were determined by GPC (Waters Alliance 150C) equipped with a refractive index detector. Three Polymer Laboratory MIXED-B columns were used in GPC analysis and 1,2,4-trichlorobenzene was used as a solvent at 160°C. The number-average and weight-average molecular weights (M_n and M_w, respectively) were obtained after polystyrene standard was calibrated. Melting temperature (T_m) was measured by DSC (Perkin-Elmer DSC-7). The protocol of DSC measurement was in the following manner. First, the sample was heated to 210°C by heating rate of 10°C/min and maintained for 5 min to remove its thermal history. Then, it was cooled to 50°C at the rate of −10°C/min and followed by reheating at 10°C/min. The thermogram of each sample was recorded in the second heating run. II of PP was obtained by boiling heptane extraction for 6 h. Tactic microstructure of polymers in terms of pentad percentage was calculated by ^{13}C-NMR spectra from methyl signals. The spectra were run on Bruker DRX-600 spectrometer operating at 150.9 MHz in *o*-dichlorobenzene-d_4 at 94°C. The instrumental conditions were as follows: pulse repetition, 0.8 s; pulse angle, 90°; scanning, approximately 15,347; spectral width, 281 ppm; temperature, 94°C; data points, −208°C.

RESULTS AND DISCUSSION

Internal donors used in this study were presented in Chart 1. In advance, catalytic performances using Cat-1 through Cat-8 were evaluated and summarized in Table I. It should be noted that Reference catalyst was prepared by diisobutyl phthalate as an internal donor. The activity data from Cat-1 through Cat-6 were not satisfied showing much lower than 22 kg-PP/g-Cat (Reference). And, even though Cat-7 and Cat-8 showed the higher activities than Reference catalyst, the bulk density data of

Table II. Propylene Polymerization with Different Catalysts

Catalyst	Internal donor	CAS No.	Activity[a]	Ti (wt %)	Ti/Mg	II[b]	M_w/M_n	T_m (°C)[c]
Reference	Diisobutyl phthalate	84-69-5	22	0.8	0.064	98.0	4.0	164.2
Cat-9	Benzoic anhydride	93-97-0	34	1.6	0.095	98.1	4.0	164.4
Cat-10	Dibenzoyl sulfide	1850-15-3	40	1.9	0.106	99.5	4.8	164.7
Cat-11	Bis(2-methylbenzoyl) sufide	59410-21-8	37	1.3	0.094	99.3	3.8	164.8
Cat-12	Bis(4-methylbenzoyl) sufide	N/A	38	1.6	0.097	99.4	3.8	164.3
Cat-13	Bis(4-chlorobenzoyl) sufide	51072-29-8	43	1.9	0.115	98.7	3.7	164.4

Polymerization condition: 2-L reactor, $C_3H_6 = 500$ g, Ti = 3.3×10^{-3} mmol, $AlEt_3 = 3$ mmol, dicyclopentyl dimethoxysilane = 0.18 mmol, 70°C, 1 h.

[a] kg of polymer/g of catalyst.

[b] Isotacticity index (weight percent of heptane insoluble fraction).

[c] Melting point temperature (second fusion; heating rate 10°C/min).

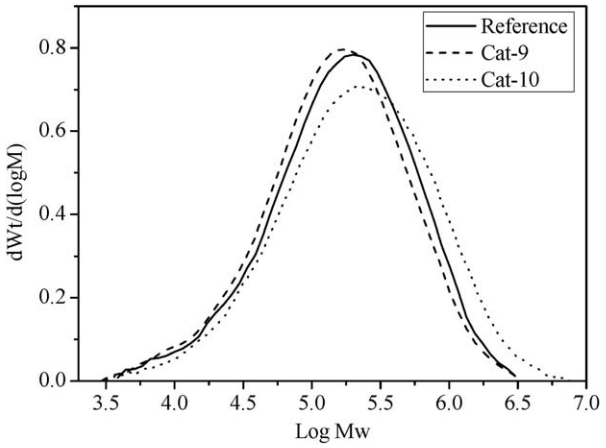

Figure 1. GPC curves of polymers obtained by (a) Reference, (b) Cat-9, and (c) Cat-10 with dicyclopentyl dimethoxysilane as the external donor.

PP product from both Cat-7 and Cat-8 were 0.42 g/mL, which is higher than 0.38 g/mL of PP synthesized from Reference catalyst. There are no correlations observed between catalytic activity and Ti content in this study.

In Table II, the performing results of benzoic anhydride, dibenzoyl sulfide, and three more sulfides[14] were presented when they were used as internal donors to synthesize PP. All five catalysts showed much greater values than Reference catalyst in activity (34–43 vs. 22 kg PP/g catalyst). In case of isotacticity indices, Cat-9 through Cat-13 showed higher values than Reference catalyst. In particular, Cat-10, Cat-11, and Cat-12 showed much higher values of 99.3–99.5 than 98.0 of Reference catalyst. Cat-10 showed even greater molecular weight distribution than that of Reference (4.8 vs. 4.0 M_w/M_n). Meanwhile, there is no significant difference in melting point of PP product.

Analytical comparison was followed mainly with three catalysts herein; Reference, Cat-9, and Cat-10 because only Cat-9 and Cat-10 satisfied major product requirements; catalytic activity of higher than 22 kg PP/g catalyst, and molecular distribution of higher than 4.0 (M_w/M_n). GPC curves of PP products from Reference, Cat-9, and Cat-10 are presented in Figure 1. It shows that PP from Cat-9 has relatively lower molecular weights but PP from Cat-10 has relatively higher molecular weights than the PP product from Reference catalyst. It should be noted that the best molecular weight distribution of PP product is achieved in the presence of Cat-10. Return to Table II, Ti contents of Reference, Cat-9, and Cat-10 were determined to 0.8, 1.6, and 1.9 wt %, respectively. It is known that Ti provides the active site adsorbed on Mg surface. Apparently it seems that Ti amount may correlate with catalytic activity. However, there are no strong evidences to support the proportional increase of catalytic activity with increasing Ti amount, which is to be explored further (refer Tables I and II). Benzoic anhydride and dibenzoyl sulfide affect PP products to have less bulky structures than PP from diisobutyl phthalate. When internal donors are being adsorbed on the Mg surface before Ti is adsorbed, this structure makes Ti adsorption easier.[1] As Cat-10 has adequately dispersed active sites, it has the highest activity among three catalysts. PP products synthesized in the presence of Reference and Cat-9 had relatively smaller amount of low-molecular-weight component. Conversely, PP product in the presence of Cat-10 has high-molecular-weight component as well as low-molecular-weight component. In Figure 2, DSC curves are presented. The peak in DSC curve represents the melting temperatures (T_m) of PP products. There is no significant difference in T_m values of PP products. In terms of the isotacticity of PP products, no significant difference was found in PP products obtained by Reference and Cat-9 (98.0 for Reference and 98.1 for Cat-9) but much higher value (99.5) in PP product synthesized by Cat-10.

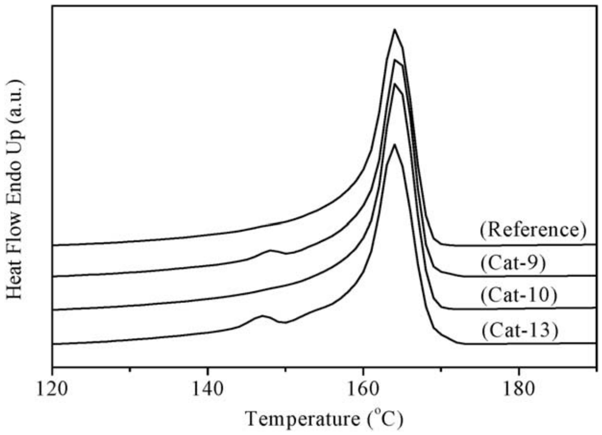

Figure 2. DSC curves (second fusion) of polymers obtained by (a) Reference, (b) Cat-9, and (c) Cat-10 with dicyclopentyl dimethoxysilane as the external donor.

The methyl regions of ^{13}C-NMR spectra of PP products are identified in Figure 3, and the data are summarized in Table III. The [mmmm] is higher in PP obtained by Cat-10 than PP products by Reference and Cat-9. It shows clearly that the structure of internal donor affects the isotacticity of PP. Here, we borrowed the concepts that were reported earlier.[16] Conceptual diagrams were presented in Figure 4. Possible coordination modes are shown in Figure 4. Bridges bound at the (110) face may be formed in two different ways in the presence of internal donor. One is that internal donor forms a bridge bound

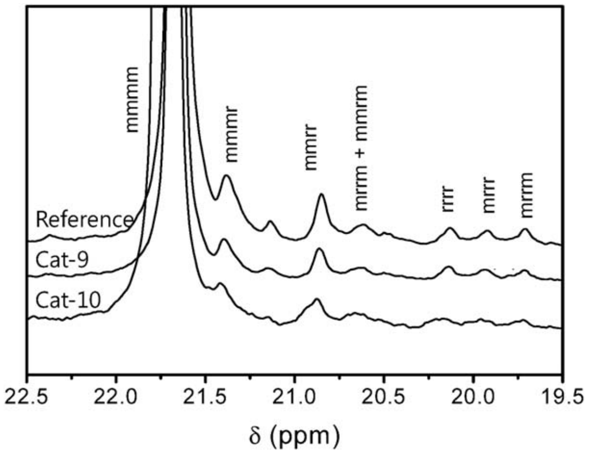

Figure 3. Methyl regions of ^{13} C-NMR spectra of PP obtained by (a) Reference, (b) Cat-9, and (c) Cat-10.

Table III. ^{13}C-NMR Stereosequence Distributions of Polypropylene A, B, and C (by Reference, Cat-9, and Cat-10)

Polymer	mmmm	mmmr	mmrr	mrrm + mmrm	rrrr	mrrr	mrrm
A	88.7	4.5	2.7	1.3	1.0	0.9	0.9
B	90.2	3.6	2.3	1.2	1.0	0.9	0.8
C	91.7	3.3	2.1	1.6	0.7	0.5	0.1

between Ti and 4-coordinated Mg ion, and the other is that internal donor lands coordinated between two 4-coordinated Mg ions. During catalyst preparation, it is known that attached internal donors on the surface of catalyst were substituted by external donors. Shen et al.[4] reported two possible attachment of external donor. If external donor forms a bridge between two 4-coordinated Mg ions, catalyst becomes active and promotes the isotacticity of PP product. Meanwhile, if external donor forms a bridge between 4-coordinated Mg ion and active Ti site, then the catalyst becomes deactivated. We hypothesize that benzoyl sulfide prefers to form a bridge bound between two 4-coordinated Mg ions (refer Figure 4), which will be discussed later. Then, subsequent introduction of external donor may either substitute or supplemented the sites that internal donors occupied during polymerization process. If this is true, external donor will form a bridge bound between two 4-coordinated Mg ions where internal donor did. This will rather promote the isotacticity of PP product. However, it needs to be explored further.

Figure 5 presents FTIR spectra of Reference, Cat-9, and Cat-10. The main regions of symmetric v (C═O) bands of dibenzoyl sulfide, benzoic anhydride, and diisobutyl phthalate are appeared at 1650–1700 cm^{-1}.[17,18] The internal donor can be adsorbed only on three types of Mg ions: 5-coordinated Mg ions at the (100) face, 4-coordinated Mg ions at the (110) face, and 3-coordinated Mg ions at the edges and the corners of MgCl$_2$ crystals.[19,20] To define the Mg surface distribution of the internal donor, the v (C═O) bands were divided in a Gaussian shape. The v (C═O) bands of benzoic anhydride and dibenzoyl sulfide exhibit two adsorption states on their surfaces with high precision. Table IV summarized the coordination values of Mg that internal donors may be possibly attached. Dibenzoyl sulfide is adsorbed on the 4- and 5-coordinated Mg ions that are dominantly placed on the activated Mg surface at 46.6 and 53.6 mol %, respectively. Benzoic anhydride is adsorbed on the 4- and 5-coordinated Mg ions at 45.0 and 55.0 mol %, respectively, such that it has lower frequency to attach on Mg surface. Conversely,

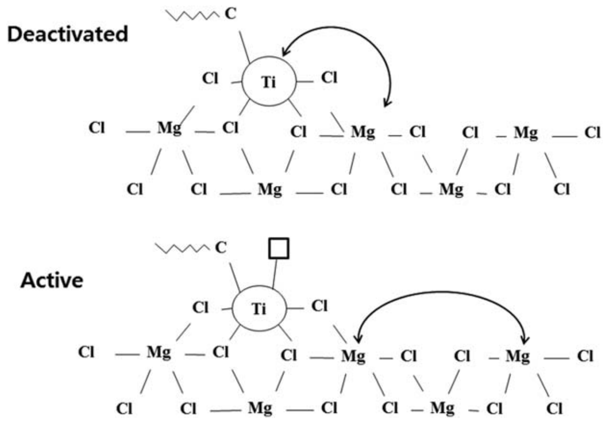

Figure 4. Schematic diagram of a possible attachment of dibenzoyl sulfide to TiCl$_4$-MgCl$_2$ template. Double arrow curves represent possible coordination modes of either internal donor or external donor.

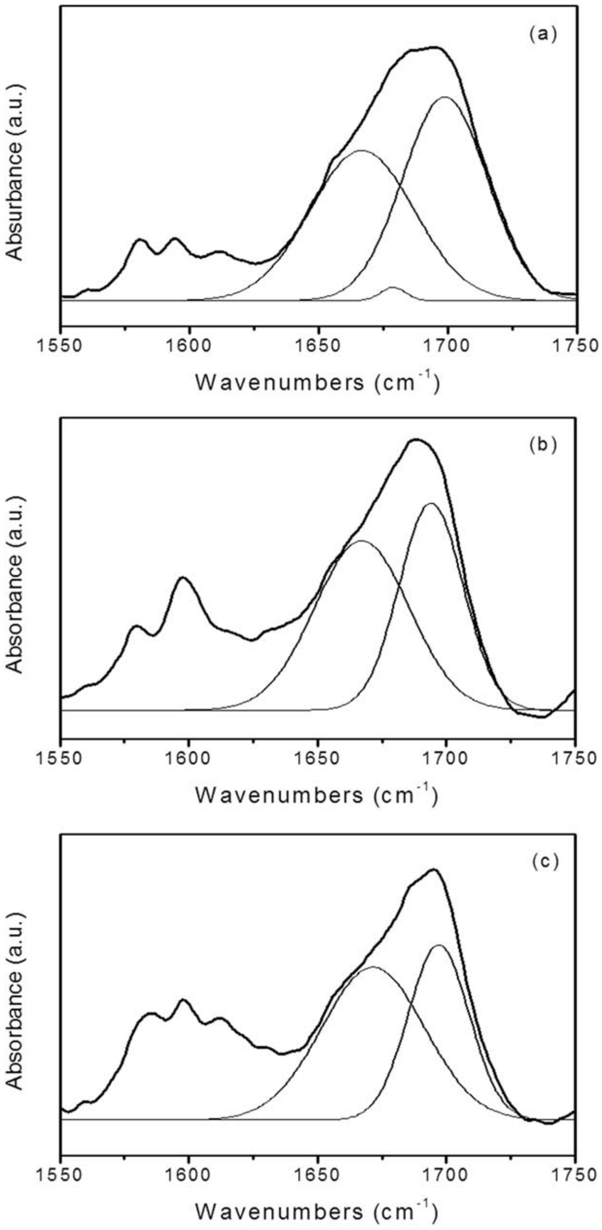

Figure 5. FTIR spectra of (a) diisobutyl phthalate, (b) benzoic anhydride, and (c) dibenzoyl sulfide adsorbed on catalyst in the v(C═O) region.

Table IV. Percentages of Mg Coordination Possibly Attached by Internal Donor

	Quantity [ν(C=O)] for surface complexes (cm $^{-1}$)(mol %)		
Catalyst	Edges or corners (3-coordinated)	(110) plane (4-coordinated)	(100) plane (5-coordinated)
Reference	3.7	40.9	55.4
Cat-9	–	45.0	55.0
Cat-10	–	46.4	53.6

diisobutyl phthalate has three adsorption states and is mainly adsorbed on 4- and 5-coordinated Mg ions at 40.9 and 55.4 mol %, respectively, and on 3-coordinated Mg ions at 3.7 mol %. It shows that the increase of attached external donors to 4-coordinated Mg ions correlates with the increase of isotacticity when compared in three catalysts (Table IV). This implies that the hypothesis may be viable.

CONCLUSIONS

PPs were synthesized in the presence of Ziegler–Natta catalyst composed of $MgCl_2$-$TiCl_4$-internal donor/AlR_3-external donor. This work is motivated by the case if we could replace current diisobutyl phthalate by a less endocrine disrupting chemical without sacrificing PP physical properties. Thirteen different catalysts modified by internal donors were examined and compared with Reference catalyst containing diisobutyl phthalate. Catalytic performance was mainly examined by catalytic activity (kg PP/g catalyst), isotacticity, and molecular weight distribution. The result was that dibenzoyl sulfide can be an alternative candidate to show the superiority to diisobutyl phthalate in the activity of catalyst (40 vs. 22 kg PP/g catalyst), the isotacticity of polymer (99.5 vs. 98.0 wt % of heptane insoluble), and the molecular weight distribution of PP product ($M_w/M_n = 4.8$ vs. 4). To interpret the superiority of benzoyl sulfide to diisobutyl phthalate, we hypothesize that the preferential bridge of benzoyl sulfide bound between two 4-coordinated Mg ions might be important to promote the isotacticity of PP product after external donor substituted the sites internal donor occupied. If this is true, external donor may continue to occupy the same sites of 4-coordinated Mg ions and save more Ti sites active. However, it needs to be examined further.

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