

MgCl₂-Supported TiCl₄ Catalysts Containing Diethyl Norbornene-2,3-Dicarboxylate Internal Electron Donor for 1-Butene Polymerization: Effects of Internal Electron Donor Configuration

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ABSTRACT: Three isomeric 5-norbornene-2,3-dicarboxylic acid diethyl ester (NDDE) with *endo*-, *exo*-, and *trans*-configuration have been synthesized and employed as internal electron donors (IED) in 1-butene polymerization over magnesium chloride supported Ziegler–Natta catalysts. It was found that the configuration of NDDE plays a key role in tuning the catalyst activity, stereospecificity, molecular weight (MW), and polydispersity index (PDI) of resulting poly(1-butene). The type of catalyst with *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid diethyl ester as IED shows the highest catalyst activity, while catalyst with *trans*-NDDE as IED yields the poly(1-butene) with the highest MW and the most broad PDI. IR results showed that the NDDE with *endo*-, *exo*-, and *trans*-configuration have different coordination way to MgCl₂, subsequently affecting the catalysts performance. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40758.

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INTRODUCTION

Electron donors (ED) play a vital role in modern MgCl₂-supported titanium Ziegler–Natta (ZN) catalyzed α -olefins stereospecific polymerization. ED regulates the catalyst activity, microstructure of resulting poly(α -olefin) including stereoregularity, molecular weight (MW), and polydispersity index (PDI), and the response to molecular hydrogen in the polymerization process.^{1–7} The evolution of the ZN catalyst is mainly attributed to new and good ED that tune the active sites to improve the performance of the catalysts.⁸ Since the fourth generation of catalysts incorporating phthalate in MgCl₂ as an integral part of the support, referred to as the internal EDs (IEDs), many kinds of organic compound have been tested as IEDs over the past decades,^{6,9–17} including 1,3-diether^{10,11} and succinates^{12,13} type IEDs. 1,3-Diether provided an extremely high activity and isotacticity in propylene polymerization even in the absence of the external EDs (EEDs) that are added during the polymerization process, while succinates showed the high catalytic activity and the wide PDI of resulting polypropylene compared to the fourth-generation catalysts.⁹ Meanwhile, phthalate is an risk to the environment and the health reported by many researches,^{18,19} so it is

an urgent in the quest for organic compounds capable of replacing phthalates as IED.

Up to now, there have been many published articles regarding the relationship between the chemical structure of IED and its effectiveness in contributing toward the stereospecificity of MgCl₂-supported ZN catalyst.^{10,13,20–26} Most of the works have been performed for propylene polymerizations. So far, only a few works concern on the influences of stereostructure of IED on the ZN catalyst performances. One example is that Chien et al. have revealed that the structural isomerism of *o*-, *m*-, or *p*-C₆H₄(COOR) aromatic diesters displayed different behaviors during the catalytic propylene polymerization process. Further work indicated two coordinated oxygen atoms of *o*-C₆H₄(COOR) have the suitable distance which is necessary to tightly coordinate to the Mg ion of the support.²⁴ The importance of the distance between the donor atoms has been identified also in the case of the 1,3-diethers-type IED.¹⁶ In the present work, three isomeric diesters derived from 5-norbornene-2,3-dicarboxylic acid with different geometric configuration, i.e. *endo*, *exo*, and *trans* (Figure 1), were synthesized and employed as IED in MgCl₂-supported Ti catalyst for 1-butene polymerization. The goals is to compare their polymerization activities, the isotactic indexes (I.I), the

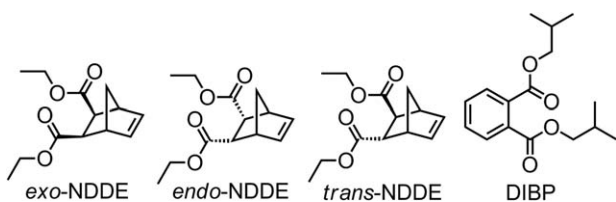


Figure 1. Internal electron donors employed to prepare MgCl_2 -supported ZN catalysts.

MW and PDI of resulting poly(1-butene) (PB), and to relate these performance parameters back to the ester structures.

EXPERIMENTAL

Materials

All manipulations of the air or moisture sensitive materials were carried out under a dry argon atmosphere with standard Schlenk techniques. Toluene was dealt with over 4 Å molecular sieves for 48 h. *Cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (*endo*-NA) was recrystallized from acetone. *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (*exo*-NA) was prepared by thermal isomerization²⁷ with purity greater than 97%. Cyclopentadiene (CPD) was prepared by the thermal cracking of dicyclopentadiene at 180°C and the distillate is collected in an ice-bath decanter to prevent the dimerization reaction. Cyclohexylmethyldimethoxysilane (CHMMS) was dried with 4 Å molecular sieve and stored under Argon. Triethylaluminum (1 mol/L in hexane). All other high-purity chemicals were purchased from Sigma-Aldrich and used as received.

Characterization

Titanium content in the catalyst was determined by spectrophotometer at 410 nm in the solution of catalyst which was treated with sulfuric acid (7.2N) on UV-CARY300 spectrometer. The MW and PDI of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6 , 10^5 , 10^4 , and 10^3 pore size in series. The measurement was performed at 150°C with 1,2,4-trichlorobenzene as the eluent with a flow rate of 1.0 mL/min. The number-average and weight average molecular weight (M_n and M_w ; respectively) values were evaluated with reference to a polystyrene standard calibration. The changes in active center distribution were studied via OriginPro 8.5.1 software based on multiple Flory functions. IR spectra of complexes and catalyst were measured on a Bruker Vector 22 spectrometer using Nujol mull at 4 cm^{-1} resolution. The I.I. of polymer was defined as a percent insoluble fraction in boiling ethyl ether extraction for 48 h. ^1H -NMR spectra of IEDs were recorded on a Bruker AV 400M in CDCl_3 .

Synthesis of Internal Electron Donors

***Cis*-5-Norbornene-2,3-dicarboxylic Acid Diethyl Ester.** The synthetic procedure is a slight modification of the published method.²⁸ A 100-mL three-necked flask equipped with reflux condenser was charged with 0.5 g of *p*-toluenesulfonic acid, 8.0 g of norbornene anhydride, and 35 mL of dried ethanol. The solution was refluxed for 24 h under CaCl_2 dry pipe protection. The ethanol was evaporated, and the slurry was extracted with

diethyl ether and washed with water. The ether phase dried over Na_2SO_4 , and concentrated on a rotary evaporator. The oily *cis*-5-norbornene-2,3-dicarboxylic acid diethyl ester was obtained by vacuum distillation.

***Cis*-5-Norbornene-*endo*-2,3-dicarboxylic acid diethyl ester (*endo*-NDDE).** Yield: 80.2%, ^1H (TMS, CDCl_3 , 400 MHz): $\delta = 6.26$ (t, 2H, $\text{CH}=\text{CH}$); $\delta = 4.06$ (m, 4H, CH_2CH_3); $\delta = 3.27$ (s, 2H, CH); $\delta = 3.15$ (s, 2H, CHCO); $\delta = 1.47$ (t, 1H, CH_2); $\delta = 1.31$ (t, 1H, CH_2); $\delta = 1.22$ (m, 6H, CH_2CH_3).

***Cis*-5-Norbornene-*exo*-2,3-dicarboxylic acid diethyl ester (*exo*-NDDE).** Yield: 71.3%, ^1H (TMS, CDCl_3 , 400 MHz): $\delta = 6.21$ (s, 2H, $\text{CH}=\text{CH}$); $\delta = 4.10$ (m, 4H, CH_2CH_3); $\delta = 3.08$ (s, 2H, CH); $\delta = 2.60$ (s, 2H, CHCO); $\delta = 2.15$ (t, 1H, CH_2); $\delta = 1.49$ (t, 1H, CH_2); $\delta = 1.48$ (m, 6H, CH_2CH_3).

***Trans*-5-Norbornene-2,3-dicarboxylic Acid Diethyl Ester (*trans*-NDDE).** The compound was synthesized according to literature process.²⁹ Yield: (60.7%), ^1H (TMS, CDCl_3 , 400 MHz): $\delta = 6.28$ (s, 1H, $\text{CH}=\text{CH}$); $\delta = 6.07$ (s, 1H, $\text{CH}=\text{CH}$); $\delta = 4.08$ (m, 4H, CH_2CH_3); $\delta = 3.36$ (s, 1H, CHCO); $\delta = 3.26$ (s, 1H, CH); $\delta = 3.12$ (s, 1H, CHCO); $\delta = 2.67$ (s, 1H, CH); $\delta = 1.61$ (t, 1H, CH_2); $\delta = 1.45$ (t, 1H, CH_2); $\delta = 1.43$ (m, 6H, CH_2CH_3).

Preparation of Metal Complexes

For the synthesis of TiCl_4 •IED complexes, TiCl_4 (0.5 mL, 50 mmol) was added dropwise to a solution of IED (1.2 g, 50 mmol) in *n*-hexane (30 mL). The TiCl_4 •IED complexes were then immediately precipitated as a bright yellow powder (the color of TiCl_4 •*trans*-NDDE complex was changed from bright yellow to dark red), the mixture were further refluxed for 1.5 h with stirring. The solvent was removed by filtration, and the residue was triply washed with 10 mL of *n*-hexane and dried in vacuum.

For the synthesis of MgCl_2 •IED complexes, anhydrous MgCl_2 (0.2 g, 2 mmol) and excess IED were placed in a 20-mL flask and the mixture stirred at 120°C for 3 h. The white precipitates obtained by adding *n*-hexane were triply washed with *n*-hexane and dried in vacuum.

Preparation of Catalyst

The catalyst synthetic procedure was analogous to methods reported. Briefly, MgCl_2 •IED and *n*-decane were added into three-neck flask and stirred for 10 min, then isooctanol were filled in at room temperature. The mixture was heated to 110°C for 3 h. TiCl_4 was added dropwise to the resulting solution (MgCl_2 •*n*ROH) at -15°C and then heated to 110°C for 1 h. After the suspension was cooled to 90°C, IED donor was again added and stirred for 30 min. The resulting precipitate was washed with *n*-hexane and toluene and then dried under vacuum. The catalysts bearing *trans*-NDDE, *endo*-NDDE, and *exo*-NDDE were designated as Cat-*trans*-NDDE, Cat-*endo*-NDDE, and Cat-*exo*-NDDE, respectively, and the catalyst bearing diisobutyl phthalate as Cat-DIBP.

1-Butene Polymerization

After a three-neck flask was purged with argon and 1-butene, 10 mg of catalyst, EED (CHMMS), H_2 (3 mL), and desired amounts of AlEt_3 were added to the reactor. Stirring the

Table I. Effect of Configuration of IED on the Ziegler–Natta Catalyst Performance for the 1-Butene Polymerization^a

| Cat | Activity (kg PB/g Ti) | I.I (%) | M_w^b ($\times 10^5$) | PDI ^b |
|-------------------------|--------------------------|---------|---------------------------|------------------|
| Cat-DIBP | 26.5 | 96.3 | 7.3 | 5.49 |
| Cat- <i>trans</i> -NDDE | 19.3 | 89.3 | 15.4 | 10.76 |
| Cat- <i>endo</i> -NDDE | 27.3 | 93.2 | 11.2 | 7.82 |
| Cat- <i>exo</i> -NDDE | 16.3 | 91.3 | 11.5 | 8.29 |

^a Polymerization conditions: $V_{(n\text{-hexane})} = 50$ mL, $m_{\text{Cat}} = 10$ mg, $\text{Al/Ti} = 300$, $\text{Al/Si} = 30$, $V_{\text{H}_2} = 3$ mL, $T = 30^\circ\text{C}$, $t = 2$ h.

^b GPC results.

mixture for 5 min at 30°C , 1-butene was fed to maintain an atmospheric pressure for 2 h. The polymerizations were quenched with acidified ethanol and the precipitates were filtered and washed by ethanol three times. The polymer was dried in vacuum at 40°C to constant weight. The I.I of PB was determined as a percent insoluble in boiling ethyl ether.

DFT Calculation

All calculations were performed using DMol3 (Materials Studio Software version 4.2 from Accelrys Inc., www.accelrys.com) program package. The geometry optimizations were performed at local density approximation level with Perdew–Wang functional (PWC) and generalized gradient approximation level with BP functional having local correlation replaced by Vosko–Wilk–Nusair (VWN) functional (VWN-BP).

RESULTS AND DISCUSSION

Three kinds of NDDE compounds with *exo*-, *endo*-, and *trans*-configurations have been used as IEDs in $\text{MgCl}_2\text{-TiCl}_4\text{-NDDE/AlR}_3\text{-CHMMS}$ catalyst systems for the polymerization of 1-butene. The Ti amounts incorporated in Cat-*exo*-NDDE, Cat-*endo*-NDDE, and Cat-*trans*-NDDE were 1.96%, 1.82%,

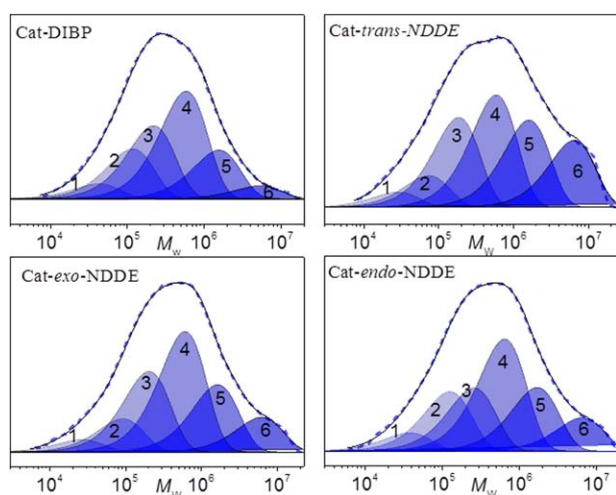


Figure 2. Molar mass distribution of a sample measured with size exclusion chromatography and its deconvolution to Flory most probable distributions that present the contribution of a single active center. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Deconvolution Result of MWD of 1-Butene Polymerization Synthesized by Different Catalyst

| Cat. | M_w ($\times 10^4$) | PDI | R | M_w ($\times 10^{-4}$) (f^b , %) | | | | | |
|-------------------------|-------------------------|-------|---------|---|---------------|---------------|---------------|----------------|---------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| Cat-DIBP | 73.39 | 5.49 | 0.99974 | 4.32 (4.88) | 11.88 (16.25) | 22.25 (23.76) | 59.24 (35.02) | 158.26 (15.80) | 541.80 (4.24) |
| Cat- <i>trans</i> -NDDE | 153.91 | 10.76 | 0.9985 | 2.90 (3.80) | 7.48 (7.86) | 18.80 (22.26) | 59.52 (27.84) | 163.46 (21.63) | 326.9 (16.61) |
| Cat- <i>endo</i> -NDDE | 112.07 | 7.82 | 0.9995 | 3.83 (5.24) | 12.75 (16.98) | 26.12 (18.08) | 65.18 (32.01) | 172.08 (18.19) | 658.66 (9.50) |
| Cat- <i>exo</i> -NDDE | 114.59 | 8.29 | 0.99954 | 2.70 (3.56) | 9.28 (9.50) | 20.60 (23.11) | 61.64 (34.53) | 165.74 (19.32) | 630.71 (9.98) |

Table III. Stretching Vibration of Carbonyl Group of IED in $\text{TiCl}_4 \bullet \text{IED}$, $\text{MgCl}_2 \bullet \text{IED}$, Adduct, and Corresponding Ziegler–Natta Catalyst^a

| IED ^a | $\text{TiCl}_4 \bullet \text{IED}$ | $\text{MgCl}_2 \bullet \text{IED}$ | Cat |
|--------------------|------------------------------------|------------------------------------|---------------------------|
| <i>Trans</i> -NDDE | 1605, 1640, 1734 | 1616, 1682, 1734 | 1620, 1682, 1728, 1757 |
| <i>Endo</i> -NDDE | 1596, 1623, 1642, 1749 | 1618, 1676, 1735(s), 1749 | 1620, 1689, 1735(s), 1752 |
| <i>Exo</i> -NDDE | 1588, 1608(w), 1628, 1749 | 1621, 1674, 1692, 1748 | 1620, 1689, 1753 |

^aNujol mull sample.

and 2.14%, respectively. It was well known that one function of IED is to affect the amount and distribution of Ti supported on the MgCl_2 , apart from controlling the morphology of MgCl_2 , which has been recognized for a long time.^{30–32}

Table I summarizes the results of 1-butene polymerizations. It was found that the activity decreases in the order of $\text{Cat-endo-NDDE} > \text{Cat-trans-NDDE} > \text{Cat-exo-NDDE}$. As expected the I.I value of resulting PB varies slightly with the type of IED employed.

The configuration of IED has an effect on MW and PDI of PB. The PBs obtained by the catalysts bearing NDDE have higher MW than that bearing DIBP. The M_w 's of PBs obtained by Cat-DIBP and Cat-trans-NDDE are 7.3×10^5 and 15.4×10^5 , respectively. Interestingly, PBs obtained by the catalysts with NDDE show broader PDIs than that by Cat-DIBP . These results indicate that the configuration of IED plays a significant role in tuning catalyst active sites distribution.

To elucidate this issue, the deconvolution of the GPC curve into individual Flory distribution curves was performed, which provides detailed information regarding the active site distribution and leads to a strong insight into the polymerization mechanism.^{33,34} It was well known that ZN catalysts contain multiple types of active centers differing in their reactivity and activity, yielding polymer molecules with different MWs and PDIs³⁴; thus the molecular weight distribution of the polymer produced by ZN catalyst can be regarded as a superposition of the distribution of each kind of active center, which is in accord with Schulz–Flory distribution with a PDI equal to 2.0. Studying the active center distribution of ZN catalyst by multiple Flory functions is a reliable method which has been proved.^{35–37} Figure 2 shows GPC curves of four PBs samples produced by four different catalysts. All GPC curves can be resolved into six Flory components with the various contents, which are named as components 1, 2, 3, 4, 5, and 6 according to the order of MW from low to high, validating that the configuration of NDDE truly takes an important operation in the active center distribution. Compared with conventional Cat-DIBP , the percentage of components 1, 2, 3, and 4 corresponding to low MW fractions decreases for Cat-exo-NDDE and Cat-trans-NDDE . However, the intensity of components 5 and 6 representing relatively high MW fractions remarkably increases, (Table II) in particular, for Cat-trans-NDDE . Note that the I.I value (see Table I) presents the opposite tendency, indicating that the active centers generating components 1 and 2 are likely made up with higher isospecific centers, while those generating components 5 and 6 contribute to lower isospecificity.

In order to better comprehend the role of IED configuration on the catalyst performances, much effort has been devoted to the investigation of interaction between the IED with other components of ZN catalysts.^{38–42} IR spectroscopy provides a very useful way to evaluate the interaction of the Mg and Ti species with an IED by comparing the carbonyl group vibrations ($\nu_{\text{C=O}}$) shift in the presence of catalyst, $\text{MgCl}_2 \bullet \text{IED}$, and $\text{TiCl}_4 \bullet \text{IED}$.^{32,38–47} As shown in Table III, Cat-trans-NDDE shows absorption peaks at 1620, 1682, 1728, and 1757 cm^{-1} . The $\nu_{\text{C=O}}$ band at 1682 cm^{-1} (shifted from 1729 cm^{-1} of pure *trans*-NDDE) arises from $\text{MgCl}_2 \bullet \text{trans-NDDE}$ (1682 cm^{-1}) and the peak at 1640 cm^{-1} of $\text{TiCl}_4 \bullet \text{trans-NDDE}$ complex disappears. The peak at 1728 cm^{-1} are assigned to the $\nu_{\text{C=O}}$ of pure *trans*-NDDE, indicating that only one C=O group of *trans*-NDDE coordinated to MgCl_2 and not to TiCl_4 in the catalyst, possibly exhibiting a very similar absorption pattern to mono-ester compounds.^{38,39,43} Thus, the PB prepared by Cat-trans-NDDE has the lowest I.I value.

The shift of $\nu_{\text{C=O}}$ bands also demonstrates that the interaction mainly occurs between *exo*-NDDE (or *endo*-NDDE) and MgCl_2 in the catalyst. Interestingly, the two peaks of $\text{MgCl}_2 \bullet \text{IED}$ at 1735 cm^{-1} and 1689 cm^{-1} are observed in the IR spectrum of Cat-endo-NDDE , while only one at 1689 cm^{-1} in Cat-exo-NDDE . No peaks indicating the existence of free NDDE appeared in Cat-endo-NDDE and Cat-exo-NDDE . These results clearly implies that *exo*-NDDE, *endo*-NDDE, and *trans*-NDDE show diverse interactions with support. Furthermore, the geometry optimized structure based on DFT calculations demonstrated that the distance between two oxygen atoms in the carbonyl groups of *trans*-NDDE is 5.179 Å, which is much longer than those of *exo* (3.502 Å) and *endo* (3.613 Å) isomers. The electrostatic potential (ESP) charges of the same oxygen atoms on the *exo* and *endo* positions were -0.445 and -0.532 , respectively, indicating that the oxygen atoms on *exo* and *endo* positions of the C=O groups would show different coordination ability to the metal from *trans*-NDDE. It is too premature to conclude on the effect of the type of NDDE on catalyst structure with the data collected here; however, it is evident that the type of NDDE influences the formation of different catalyst structures, and thus 1-butene polymerization behavior.

CONCLUSIONS

Three different ZN catalysts were prepared by employing *endo*-NDDE, *exo*-NDDE, and *trans*-NDDE as IED and 1-butene polymerizations were performed by using the resulting catalysts. The configuration of IED significantly affects the catalyst activity, MW, PDI, and isotacticity of the catalyst. The NDDE compounds mainly coordinate to MgCl_2 , not to TiCl_4 . PB obtained from

Cat-*trans*-NDDE showed the highest M_w and PDI values, while Cat-*endo*-NDDE showed best catalyst activity and isospecificity.

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