

The influence of combined external donor and combined cocatalyst on propylene polymerization with a MgCl₂-supported Ziegler–Natta catalyst in the presence of hydrogen

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ABSTRACT: The influence of combined external donor (ED) (diphenyldimethoxysilane/dicyclopentylmethoxysilane) and combined cocatalyst (triethylaluminum/triisobutylaluminum) on propylene polymerization with MgCl₂-supported Ziegler–Natta catalyst in the presence of hydrogen was investigated. By deconvolution analysis of the molecular weight distribution (MWD) into multiple Flory components, the influence of ED and cocatalyst on the active center distribution of the catalyst was demonstrated, and the mechanism was discussed. Using combined cocatalyst and combined donor, iPP with high molecular weight, high isotacticity index, and broad MWD can be obtained. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41689.

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INTRODUCTION

In industry, the fourth-generation Ziegler–Natta catalyst that polypropylene (PP) is typically manufactured by is generally prepared from TiCl₄ supported by MgCl₂, and combined with an internal donor (ID), a cocatalyst, and an external donor (ED), and polymerization is carried out in the presence of hydrogen. The molecular structure and performance of the obtained PP are dominantly controlled by ID, ED, cocatalyst, and hydrogen.^{1–9}

PP can be isotactic, syndiotactic, or atactic, which distinguish from the orientation of the pendant methyl groups attached to the backbone. Isotactic PP has the highest crystallinity, resulting in good mechanical and chemical properties such as stiffness, tensile strength, and excellent chemical resistance. Syndiotactic PP is less stiff than isotactic PP but with better impact strength and toughness. Atactic PP is even an amorphous or waxy material; thereby, it is poor in the physical and chemical properties. From the view of applications of PP, to control the composition and structure of PP and establish the balance of stiffness and toughness is very important.^{10–12}

By the fourth-generation Ziegler–Natta catalyst, PP with an isotactic index of 99% or even higher can be produced at rather high activity. In the last decade, various types of EDs have been studied

but only a few researches on combined ED.^{13–19} It is found that using combined ED can regulate the molecular weight distribution (MWD), melt index, and the physical properties of PP. Vyas *et al.* used dimethyldimethoxysilane, diisopropyldimethoxysilane, and dicyclopentylmethoxysilane (DCPDMS) to study the effect of dialkyl group of the EDs. They found that the microstructure and molecular weights of the resultant PP were affected by the combination of ED.²⁰ Georgellis *et al.* studied a new catalyst system with mixed EDs (tetraethoxysilane and DCPDMS).²¹ This catalyst system has been found to be effective in making PP and PP copolymers with relatively high melt flow rates and moderately broad MWD. Chang *et al.* studied the effect of the different mixed EDs (cyclohexylmethyldimethoxysilane, *n*-propyltriethoxysilane, tetraethoxysilane, dicyclohexyldimethoxysilane (DCPDMS), and dipiperidinedimethoxysilane) on the sequence length distribution of PP prepared by Ziegler–Natta catalysts using successive self-nucleation and annealing technology (SSA).²² The SSA results showed that the difference of mixed donors significantly affected the crystallization ability and the relative contents of long isotactic sequence length. Harding and van Reenen studied PP prepared with a Ziegler–Natta catalyst using two different EDs diphenyldimethoxysilane (DDS) and methylphenyldimethoxysilane (MPDMS), and the results showed that DDS exerted greater influence on the active sites and the microstructure of PP than MPDMS did.²³ Previously, we have found

Table I. Homopolymerization of Propylene Prepared by TEA/TIBA/DDS/DCPDMS^a

| Entry | Cocat. (TEA : TIBA) | External donor (DDS : DCPDMS) | Activity ^b | I.I. ^c (wt %) | C7-insol. | | C7-sol. | |
|-------|---------------------|----------------------------------|-----------------------|--------------------------|-----------|------------------|---------|-----|
| | | | | | M_w^d | PDI ^e | M_w | PDI |
| E4B0S | 4 : 0 | 3 : 0 | 1.9 | 98.3 | 15.2 | 4.2 | 0.53 | 2.0 |
| E4B1S | 4 : 1 | 3 : 0 | 2.0 | 98.3 | 18.0 | 4.4 | 1.03 | 2.9 |
| E4B2S | 4 : 2 | 3 : 0 | 1.9 | 97.5 | 18.4 | 4.3 | 1.05 | 2.0 |
| E4B3S | 4 : 3 | 3 : 0 | 2.0 | 97.6 | 18.7 | 4.0 | 1.10 | 3.0 |
| E4B4S | 4 : 4 | 3 : 0 | 1.9 | 97.6 | 20.0 | 3.8 | 1.84 | 4.1 |
| E4B0D | 4 : 0 | 0 : 3 | 1.8 | 99.2 | 23.5 | 4.2 | 0.56 | 2.1 |
| E4B1D | 4 : 1 | 0 : 3 | 1.6 | 99.1 | 28.0 | 4.6 | 0.58 | 2.2 |
| E4B2D | 4 : 2 | 0 : 3 | 1.7 | 98.9 | 27.9 | 4.1 | 0.58 | 2.3 |
| E4B3D | 4 : 3 | 0 : 3 | 1.7 | 98.8 | 29.4 | 4.8 | 0.64 | 2.2 |
| E4B4D | 4 : 4 | 0 : 3 | 1.9 | 98.8 | 35.2 | 4.3 | 0.74 | 2.2 |
| S3D0E | 4 : 0 | 3 : 0 | 1.9 | 98.3 | 15.2 | 4.2 | 0.53 | 2.0 |
| S3D1E | 4 : 0 | 3 : 1 | 1.7 | 98.3 | 23.0 | 5.6 | 0.56 | 2.0 |
| S3D3E | 4 : 0 | 3 : 3 | 1.8 | 98.9 | 25.7 | 5.3 | 0.41 | 1.6 |
| S1D3E | 4 : 0 | 1 : 3 | 1.6 | 98.7 | 27.7 | 4.9 | 0.38 | 1.7 |
| E4B1 | 4 : 1 | 7 : 3 | 1.7 | 99.0 | 28.6 | 4.6 | 0.53 | 2.1 |
| E4B4 | 4 : 4 | 7 : 3 | 1.9 | 99.2 | 36.9 | 4.5 | 0.53 | 1.9 |

^aPolymerization condition: prepolymerization stage: 40–50 mg catalyst, $P_{Pr} = 0.09375$ MPa, $P_{H_2} = 0.00625$ MPa, $t = 15$ min, $T = 25^\circ\text{C}$; homopolymerization stage: $P_{Pr} = 0.594$ MPa, $P_{H_2} = 0.006$ MPa, $t = 2$ h, $T = 75^\circ\text{C}$.

^bkgPP/gcat.

^cI.I. = weight percentage of C7-insol. in the initial PP.

^dWeight average molecular weight, in 10^4 g/mol, determined by GPC.

^ePDI = Polydispersity index.

that the composition and structure of PP synthesized by a MgCl_2 -supported Ziegler–Natta catalysts were strongly affected by the type of cocatalyst.^{24–28} The molecular weight and isotacticity index were significantly affected by the steric hindrance of alkylaluminum. But, there is no report on using combined ED and combined cocatalyst together in propylene polymerization with MgCl_2 -supported Ziegler–Natta catalyst.

In this work, the influence of combined ED (DDS/DCPDMS) and combined cocatalyst ($\text{AlEt}_3/\text{Al}(i\text{-Bu})_3$) on propylene polymerization with a MgCl_2 -supported Ziegler–Natta catalyst in the presence of hydrogen was investigated. The influence of ED and cocatalyst on the active center distribution of the catalyst was demonstrated, and the mechanism was discussed.

EXPERIMENTAL

Chemicals

A commercial spherical MgCl_2 -supported Ziegler–Natta catalyst ($\text{MgCl}_2/\text{Di}/\text{TiCl}_4$, Ti content = 2.7 wt %, produced by SINOPEC) containing a diester type ID was used for polymerization. Propylene (polymerization grade, supplied by Yangzi Petrochemical Co., Nanjing, China) was purified by passing through columns of molecular sieve and manganese-based deoxygen agent in a gas purification system made by Dalian Samat Chemicals Co. Hydrogen (supplied by Yangzi Petrochemical Co., Nanjing, China) was purified by passing through columns of molecular sieve and manganese-based deoxygen agent in a gas purification system made by Dalian Samat Chemicals Co. Tri-

ethylaluminum (TEA, purchased from Albemarle Co.) was used as received and diluted in *n*-heptane before use. Triisobutylaluminum (TIBA, purchased from Albemarle Co.) was used as received and diluted in *n*-heptane before use. *n*-Heptane was first dried over 4 Å molecular sieves under dry N_2 and then refluxed over Na before use. DDS (purchased from Huabang Chemistry, Hubei, China) was distilled before use. DCPDMS (purchased from Huabang Chemistry, Hubei, China) was distilled before use.

Homopolymerization of Propylene

To obtain flowable PP particles, PP homopolymer was prepared by a two-stage polymerization process in an 800-mL Büchi autoclave with a helical stirrer. The pressure of propylene (containing 6.25 mol % H_2) in the prepolymerization stage was 1 atm, and the polymerization temperature was 25°C . One hundred milliliter of *n*-heptane used as solvent, a designated amount of cocatalyst ($\text{Al}/\text{Ti} = 100$) and EDs ($\text{Si}/\text{Ti} = 5$) were added into the autoclave successively. One minute later, 40–50 mg of MgCl_2 -supported Ziegler–Natta catalyst was added into the autoclave to start the polymerization. The mechanical stirring speed was about 300 rpm. Fifteen minutes later, propylene containing 1 mol % H_2 was introduced into the autoclave. Propylene homopolymerization was carried out at 0.6 MPa and 75°C . Ten minutes later, the mechanical stirring speed was adjusted to 100 rpm. The polymerization was continuously carried out for 110 min. Finally, unreacted propylene and solvent were removed by vacuum, and the solid product was poured

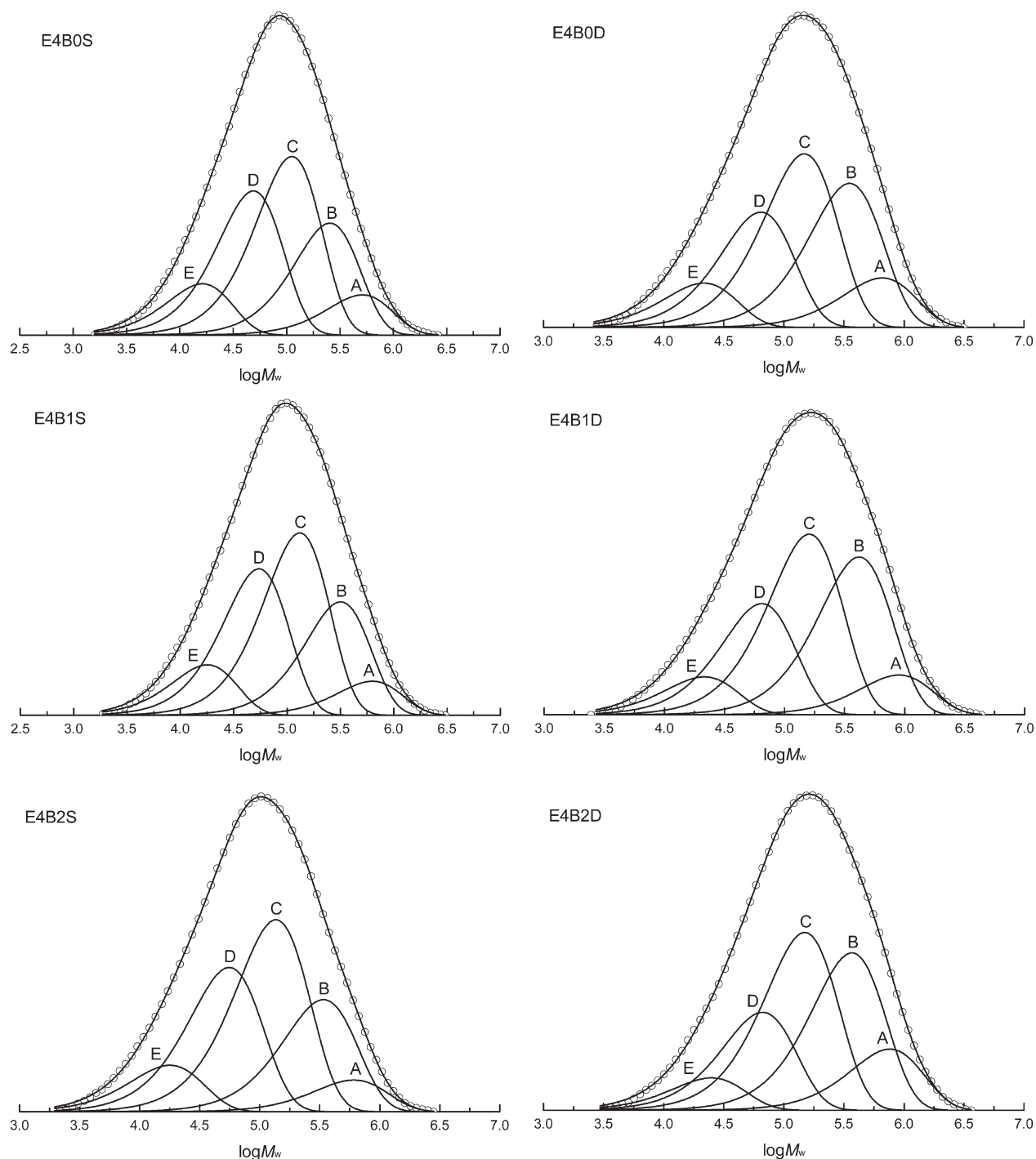


Figure 1. GPC curves of C7-insol. fraction and their deconvolution into multiple Flory components.

into an excess of ethanol containing 5% HCl, filtered and washed with ethanol three times. The resultant PP was dried in a vacuum at 60°C for 12 h.

Determination of the Isotacticity Index of PP

About 1 g of PP was extracted by boiling *n*-heptane for 12 h. The *n*-heptane soluble part (C7-sol.) was recovered by rotary evaporation. The *n*-heptane insoluble part (C7-insol.) was dried

in a vacuum. The isotacticity index (I.I.) of PP was calculated as the weight percentage of C7-insol. in the initial PP.

Measurement of the Molecular Weight

The molecular weights and MWD of the fractions were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories, Church Stretton, United Kingdom) at 150°C in 1,2,4-trichlorobenzene with 0.0125% butylatedhydroxy toluene (BHT). Three PL mixed B

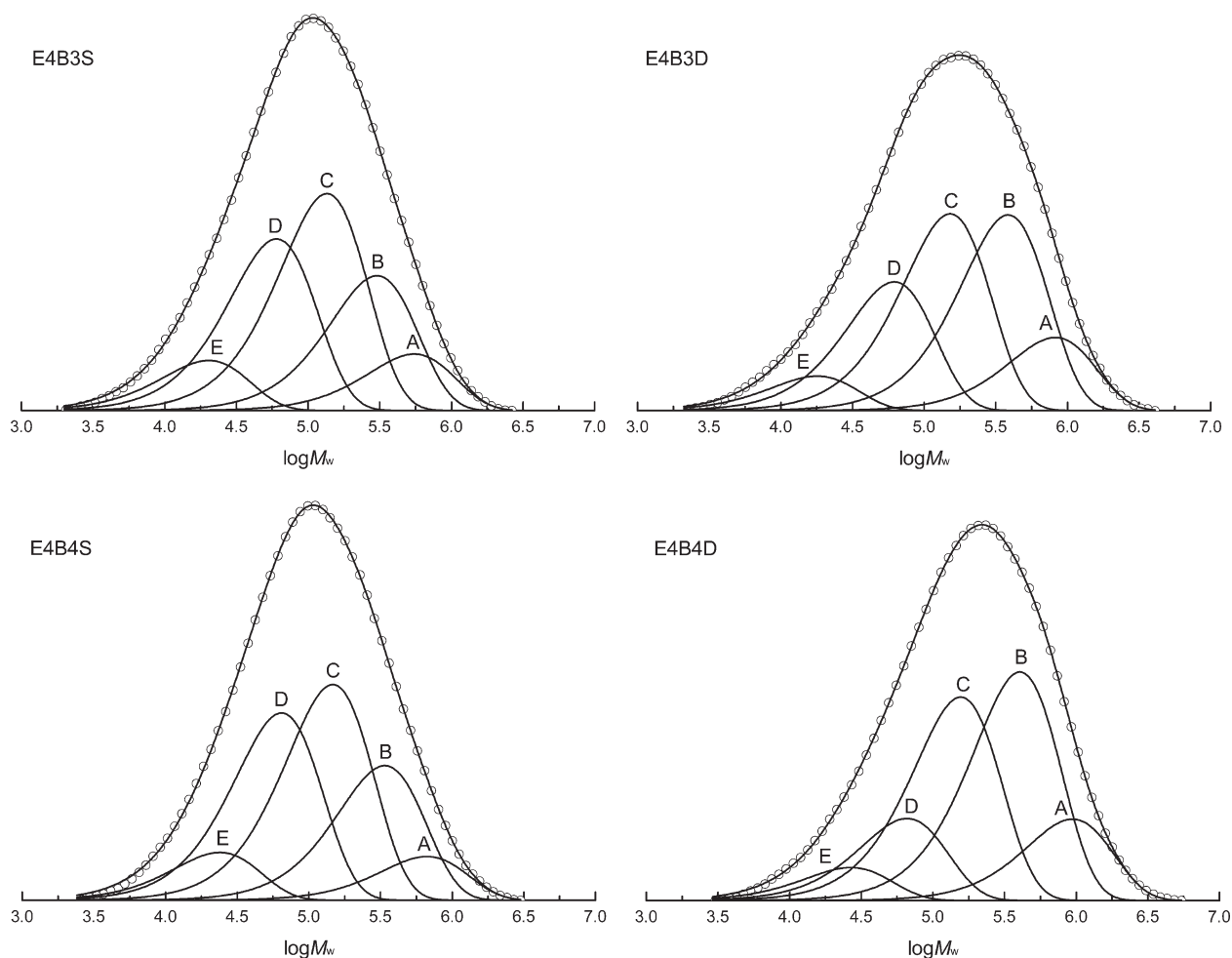


Figure 1. Continued.

columns (500–10⁷) were used. Universal calibration against narrow polystyrene standards was used.

Deconvolution of Polymer MWD by Multiple Flory Functions

Because multiple active centers are present in TiCl₄/MgCl₂/ID type supported Ziegler–Natta catalysts, deconvolution of polymer MWD by multiple Flory functions^{29–33} is an effective method to study the active center distribution of the catalyst.^{34,35} By the same way described in our previous work,^{26,36,37} the GPC curves of C7-insol. fraction of all the samples were deconvoluted into five Flory “most-probable” distribution peaks. Each Flory component corresponded to a certain type of active center, thus, there were five types of active centers, C_A^{*}, C_B^{*}, C_C^{*}, C_D^{*}, and C_E^{*} in the catalysis systems according to the sequence of molecular weight from high to low. According to the difference in molecular weight, the active centers could be divided into three kinds: C_A^{*} + C_B^{*} represented the active center producing high molecular weight PP, C_C^{*} represented the active center producing medium molecular weight PP, and C_D^{*} + C_E^{*} represented the active center producing low molecular weight PP.

RESULTS AND DISCUSSION

Effects of Combined Cocatalyst on Propylene Polymerization

To investigate the influences of cocatalyst on propylene polymerization, the mixture of TEA and TIBA (TEA/TIBA = 1 : 0–1 : 1,

Al/Ti = 100) was used as cocatalyst and DDS or DCPDMS (Si/Ti = 5) was added as external electron donor, respectively. The polymerization results were summarized in Table I (E4B0S–E4B4S, E4B0D–E4B4D).

As shown in Table I, compared with DCPDMS, using DDS as ED, the catalyst exhibited higher activity but produced PP with lower isotacticity index. As the amount of TIBA in TEA/TIBA mixture increased, the isotacticity index of the resultant PP decreased, which was independent of the type of ED but the catalytic activity tended to increase, and the molecular weight of both C7-insol. and C7-sol. tended to increase. In this type of polymerization, the polymer molecular weight is primarily dependent on hydrogen response, that is, the sensitivity of the catalyst to chain transfer with hydrogen rather than chain transfer with monomer or with aluminum.^{3,4} The hydrogen response is mainly dependent on catalyst regioselectivity, that is, the relative incidence of primary (1,2-) and secondary (2,1-) monomer insertion, as has been demonstrated in various publications.^{5–9} In our system, the amount of hydrogen was not changed, so differences between the polymers obtained may be due to the use of different cocatalysts.

Titanium catalysts, after activation, contain both trivalent and divalent species, of which Ti²⁺ species are active only for

Table II. Results of GPC Analysis and Deconvolution by Flory Components

| Entry | M_w^a | PDI ^b | C_A^* | | C_B^* | | C_C^* | | C_D^* | | C_E^* | |
|-------|---------|------------------|-------------------|-------|---------|-------|---------|-------|---------|-------|---------|-------|
| | | | Fr % ^c | M_w | Fr % | M_w | Fr % | M_w | Fr % | M_w | Fr % | M_w |
| E4B0S | 15.2 | 4.2 | 7.7 | 52.1 | 21.3 | 25.8 | 34.0 | 11.2 | 27.4 | 4.9 | 9.6 | 1.6 |
| E4B1S | 18.0 | 4.4 | 6.5 | 64.1 | 21.6 | 32.4 | 34.7 | 13.2 | 27.8 | 5.4 | 9.4 | 1.8 |
| E4B2S | 18.4 | 4.3 | 6.0 | 61.7 | 21.3 | 34.6 | 36.5 | 13.7 | 27.4 | 5.5 | 8.7 | 1.8 |
| E4B3S | 18.7 | 4.0 | 9.0 | 56.0 | 21.4 | 30.7 | 34.5 | 13.6 | 27.3 | 6.0 | 7.8 | 2.0 |
| E4B4S | 20.0 | 3.8 | 7.0 | 67.6 | 21.4 | 34.4 | 34.3 | 14.8 | 29.7 | 6.4 | 7.5 | 2.4 |
| E4B0D | 23.5 | 4.2 | 9.4 | 67.0 | 27.4 | 35.8 | 33.0 | 15.0 | 21.9 | 6.4 | 8.2 | 2.2 |
| E4B1D | 28.0 | 4.6 | 7.5 | 91.3 | 30.0 | 42.6 | 34.3 | 16.3 | 21.1 | 6.5 | 7.0 | 2.2 |
| E4B2D | 27.9 | 4.1 | 11.6 | 77.4 | 30.0 | 37.5 | 33.8 | 15.1 | 18.6 | 6.6 | 6.0 | 2.5 |
| E4B3D | 29.4 | 4.8 | 11.7 | 83.5 | 31.2 | 39.2 | 31.3 | 15.3 | 20.5 | 6.2 | 5.4 | 1.8 |
| E4B4D | 35.2 | 4.3 | 13.0 | 95.7 | 36.4 | 41.2 | 32.4 | 15.8 | 13.0 | 6.6 | 5.2 | 2.7 |
| S3D0E | 15.2 | 4.2 | 7.7 | 52.1 | 21.3 | 25.8 | 34.0 | 11.2 | 27.4 | 4.9 | 9.6 | 1.6 |
| S3D1E | 23.0 | 5.6 | 7.3 | 89.7 | 24.9 | 37.3 | 33.4 | 13.8 | 25.1 | 5.4 | 9.3 | 1.7 |
| S3D3E | 25.7 | 5.3 | 8.5 | 89.3 | 29.1 | 37.5 | 33.6 | 14.0 | 21.7 | 5.5 | 7.0 | 1.7 |
| S1D3E | 27.7 | 4.9 | 9.5 | 88.6 | 30.3 | 39.3 | 33.4 | 14.6 | 20.5 | 5.7 | 6.4 | 1.9 |
| S0D3E | 23.5 | 4.2 | 9.4 | 67.0 | 27.4 | 35.8 | 33.0 | 15.0 | 21.9 | 6.4 | 8.2 | 2.2 |
| E4B1 | 28.6 | 4.6 | 10.6 | 85.5 | 31.7 | 39.0 | 32.7 | 14.5 | 19.1 | 6.2 | 6.0 | 2.1 |
| E4B4 | 36.9 | 4.5 | 14.5 | 98.9 | 35.2 | 41.7 | 31.8 | 15.6 | 13.5 | 6.6 | 5.0 | 2.5 |

^aWeight average molecular weight, in 10^4 g/mol.^bPDI = Polydispersity index.^cFr % was the weight percentage of the fraction produced on a certain active center in the whole product.

ethylene and Ti^{3+} species are normally active for both ethylene and propylene.^{38,39} If the growing polymer chain end is an ethylene unit, the Ti^{2+} species can also effect the addition of propylene.⁴⁰ TIBA has lower Lewis acidity and higher steric hindrance than TEA, limiting its association with the active sites. It also has lower reducing power than TEA, so the proportion of Ti^{3+} species present may be higher with TIBA than with TEA, leading to higher catalytic activity. When the catalyst is brought into contact with TEA, a large proportion of the ID is lost as a result of alkylation and/or complexation reaction. To a large extent, the ED replaces the ID in the solid catalyst, thereby maintaining high catalyst stereospecificity.⁴¹ As TIBA has lower reduction power but higher steric hindrance than TEA, the former can extract less ID than the latter. Thus, using the former as ED, less ID can be replaced which results in lower catalyst stereospecificity.

Compared with DDS, the PP produced with DCPDMS had higher molecular weight. For alkoxysilanes $[R_2(CH_3O)_2Si]$, R = cyclopentyl (Cpy), phenyl (Ph), etc.), Cpy is bulkier than Ph. That is, the steric hindrance of DCPDMS is greater than that of DDS and it has been demonstrated that the use of DCPDMS leads to the formation of highly stereo- and regio-specific active sites and the formation of a high molecular weight polymer fraction.⁵⁻⁹

Extracted by boiling *n*-heptane, PP could be divided into two parts, namely *n*-heptane soluble part (C7-sol.) and *n*-heptane insoluble part (C7-insol.). C7-sol. contained mainly atactic PP and/or low isotactic PP. C7-insol. was mainly isotactic PP. Interestingly, as the amount of TIBA in TEA/TIBA mixture increased, the molecular weights of C7-sol. fraction increased

gradually which was independent of the type of ED. However, in the case of the polydispersity index (PDI) of the soluble fractions, using DDS as ED, as the amount of TIBA in TEA/TIBA mixture increased, the PDI values tended to increase. But in the presence of DCPDMS, the introduction of TIBA hardly influenced the PDI values (Figure 1).

Table II shows the relative proportions and weight average molecular weights (M_w) of the individual Flory components. According to Table II, compared with DDS, the presence of DCPDMS led to higher Fr % values of ($C_A^* + C_B^*$), similar Fr % values of C_C^* and lower Fr % values of ($C_D^* + C_E^*$). Namely, DCPDMS was a more efficient agent to deactivate aspecific sites and/or convert aspecific sites into isospecific sites.⁴²

In the case of DDS, as the amount of TEA in the TEA/TIBA mixture increased, the Fr % values of C_E^* decreased, but the Fr % value of the other active centers changed slightly. It indicated that TIBA could suppress the activity of C_E^* and/or convert C_E^* into the other active centers. This resulted in a slight increase in the molecular weight of the C7-insol. fraction. In the case of DCPDMS, as the amount of TIBA in TEA/TIBA mixture increased, the Fr % values of ($C_A^* + C_B^*$) increased and the Fr % values of ($C_D^* + C_E^*$) decreased. Therefore, the molecular weight of C7-insol. fraction increased significantly. It indicated that combining with DCPDMS TIBA was more efficient to convert ($C_D^* + C_E^*$) into ($C_A^* + C_B^*$).

Effects of Combined External Donor on Propylene Polymerization

The mixtures of DDS and DCPDMS (DDS/DCPDMS = 1 : 0–1 : 1, Si/Ti = 5) were used as ED and TEA or TIBA (Al/Ti = 100)

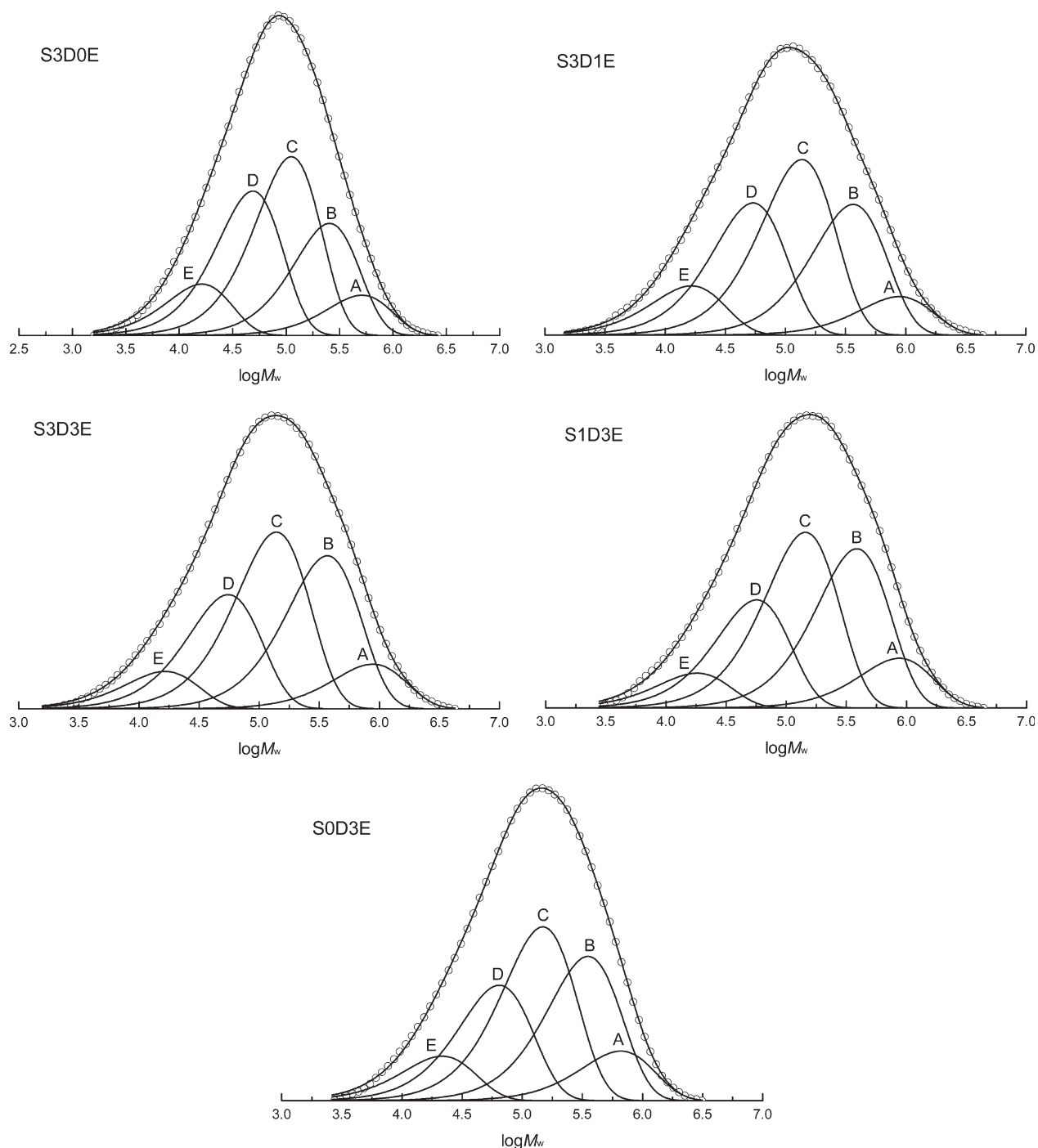


Figure 2. GPC curves of PP-C7-insoluble fraction and their deconvolution into multiple Flory components.

was added as cocatalyst, respectively. The polymerization results were listed in Table I (S3D0E–S1D3E).

According to Table I, as the amount of DCPDMS in DDS/DCPDMS mixture increased, the isotacticity indexes and molecular weights of PP increased. But, the catalytic activity did not change much.

The polymers in Table I were divided into two fractions by boiling *n*-heptane. At DDS : DCPDMS = 1 : 3, the molecular weight of the C7-sol. fraction was the lowest, while the molecu-

lar weight of the C7-insol. fraction was the highest. It is apparent from the data in Tables I and II that, using a mixture of the two EDs, PP with high molecular weight and broad MWD could be obtained.

To investigate the influence of combined ED on active center distribution, the GPC curves of C7-insol. fraction were also deconvoluted into five Flory components, respectively. The results are shown in Figure 2 and summarized in Table II. At DDS : DCPDMS = 1 : 3, the Fr % value of ($C_A^* + C_B^*$) was the

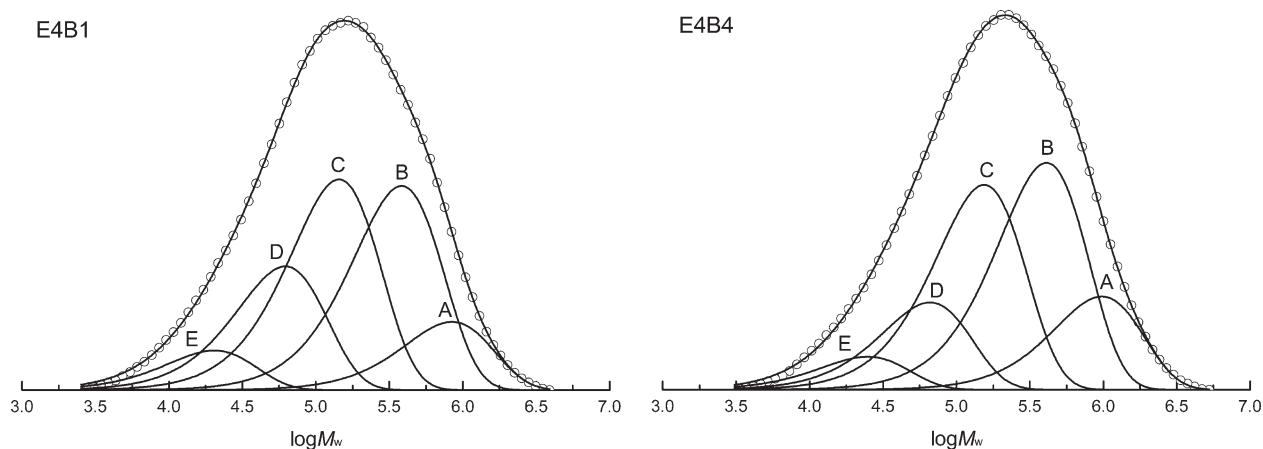


Figure 3. GPC curves of C7-insol. fraction and their deconvolution into multiple Flory components.

highest, and the Fr % value of $(C_D^* + C_E^*)$ was the lowest. But, the introduction of DCPDMS did not affect the Fr % value of C_C^* . The results indicate that a DDS/DCPDMS mixture containing a relatively high proportion of DCPDMS is most efficient in converting $(C_D^* + C_E^*)$ into $(C_A^* + C_B^*)$.

Effects of Combined Cocatalyst and Combined External Donor on Propylene Polymerization

As stated above, using a TEA/TIBA mixture as cocatalyst or using a DDS/DCPDMS mixture as ED, PP with higher molecular weight and broad MWD could be produced. In this section, the TEA/TIBA mixture and the DDS/DCPDMS mixture were introduced into propylene homopolymerization together. The influence of combined cocatalyst and combined ED on propylene homopolymerization was investigated. As the hydrogen sensitivity of DCPDMS was quite low, it is hard to control the molecular weight of product. To satisfy the requirements of industrial applications, in these experiments, the molar ratio between DDS and DCPDMS was set as DDS/DCPDMS = 7 : 3. The polymerization results are summarized in Table I (E4B1–E4B4).

It is apparent that the isotacticity index of PP prepared with combined cocatalyst and combined ED was very high. At TEA : TIBA = 4 : 4 and DDS : DCPDMS = 7 : 3, the isotacticity index of PP was the same as that prepared using DCPDMS alone as ED. Meanwhile, the introduction of combined cocatalyst and combined ED did not affect the catalytic activity significantly.

The GPC curves of C7-insol. fraction are shown in Figure 3. These two curves were also deconvoluted into five Flory components. The results are summarized in Table II. As the amount of TIBA in TEA/TIBA mixture increased, the Fr % value of $(C_A^* + C_B^*)$ increased, but the Fr % value of $(C_D^* + C_E^*)$ decreased. Namely, although there were two types of ED existed in the polymerization, these two EDs did not prevent TIBA from converting $(C_D^* + C_E^*)$ into $(C_A^* + C_B^*)$.

CONCLUSIONS

ED and cocatalyst can significantly affect propylene polymerization with a $MgCl_2$ -supported Ziegler–Natta catalyst. The active

center distribution of the catalyst can be regulated by varying the feed ratio between TEA and TIBA as well as between DDS and DCPDMS. As a result, the molecular structure of the resultant PP can be controlled to some extent. Partial replacement of TEA by TIBA led to higher PP molecular weight. In combination with DCPDMS, TIBA was more efficient to convert $(C_D^* + C_E^*)$ (the active centers producing low molecular weight PP) into $(C_A^* + C_B^*)$ (the active centers producing high molecular weight PP). Using a DDS/DCPDMS mixture as ED, PP with high molecular weight and broad MWD could be produced, a relatively high proportion of DCPDMS being most efficient in converting $(C_D^* + C_E^*)$ into $(C_A^* + C_B^*)$. These characteristics, and in addition high isotacticity index, were also obtained using combined cocatalyst and combined ED.

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