Influences of silane/ether composite external donors on propylene polymerization with MgCl$_2$-supported Ziegler-Natta catalyst in the presence of hydrogen

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Abstract: In this work, the effects of two silane type external donors, Ph$_2$Si(OCH$_3$)$_2$ (DPDMS) and dicyclopentyldimethoxysilane (DCPDMS) on propylene slurry polymerization in the presence of hydrogen with a MgCl$_2$/TiCl$_4$/DIBP-Al(C$_2$H$_5$)$_3$ catalyst system were investigated, and the tacticity distribution and molecular weight distribution (MWD) of polypropylene (PP) were further regulated by using silane/ether (ROCH$_3$, R = n-Bu, i-C$_8$H$_{17}$) composite external donors. The tacticity distribution of PP, as revealed by successive self-nucleation and annealing (SSA) thermo analysis of the polymer, is markedly changed by the external donors. DCPDMS shows much stronger effects than DPDMS. Addition of the ether as an auxiliary external donor in MgCl$_2$/TiCl$_4$/DIBP-TEA/silane (DPDMS or DCPDMS) lead to further increase in catalytic activity and isotacticity of PP, and changes in tacticity distribution. By using the composite external donors, PP with both higher isotacticity index, lower molecular weight or narrower molecular weight distribution was prepared at high activity. Effects of the external donors on the active center distribution were discussed based on the results of deconvoluting the MWD curve with multiple Flory “most-probable” distributions, and possible mechanism of the external donor effects was proposed.

Introduction

High-activity MgCl$_2$-supported Ziegler-Natta catalysts play a dominant role in the industrial production of isotactic polypropylene (PP). In this type of catalyst, electron donating compounds called internal donors (ID) are usually added to improve the stereospecificity. So called “external” electron donors are also added in the polymerization system together with the cocatalyst triethyl aluminum (TEA) [1]. When the catalyst contains ester type internal donor (usually a phthalate), use of an external donor is a necessity to ensure high isotacticity of PP [2]. By using external donors, PP with an isotactic index of 99% or higher can be produced at rather high activity. In the last decades, various types of external donors have been studied, and alkoxysilanes were found to be better than the others in words of isotacticity and polymerization activity [3, 4].

However, the so-called isotacticity index (I.I.), which is the fraction of PP insoluble in cold xylene or boiling n-heptane, reflects only roughly the chain structure of PP. In fact, when the PP sample is fractionated by temperature rising elution fractionation (TREF), a rather broad distribution of fractions can be observed. The TREF fractions eluted at different temperature have different crystallinity, which is determined by the amount of stereo defects in the PP chains. PP chains with higher content of stereo
defects are eluted at lower temperature. This means that PP synthesized with supported Ziegler-Natta catalysts is composed of a series of chains of different stereoregularity, and the isotacticity index only reflects the total amount of PP chains of medium to high isotacticy. In the studies of external donor effects, information of the chain structure distribution is even more important than the isotacticity index. As reported by Chadwick J. C. et al [5,6], changing the external donor from cyclohexyl(methyl)-dimethoxysilane (CHMDMS) to dicyclopentyldimethoxysilane (DCPDMS) in propylene polymerization with a MgCl₂/TiCl₄/DIBP catalyst caused not only an increase in the polymer’s isotacticity index, but also a remarkable shift of the TREF peak to the high temperature end. This means that raising PP isotacticy by using alkoxy silane external donor with bulky alkyl groups is usually accompanied by increase in the stereoregularity of all the polymer chains. Such a feature of external donor effect will form an unfavorable limitation to modification of PP properties by application of external donors, because the properties of PP is not only influenced by its atactic fraction (i.e. the fraction soluble in cold xylene or boiling n-heptane), but more dominantly, by the entire distribution of tacticity among the polymer chains. For this reason, it is necessary to find new type of external donors that can not only improve the isotacticity of PP, but also its tacticity distribution.

In the most important applications of PP, the atactic fraction, which is an amorphous or waxy material, is harmful to the physical and mechanical properties. Reducing this kind of fraction in PP is usually beneficial. However, the stereoregularity of the “isotactic” part, which determine the crystallinity and therefore the physical properties of PP, is not necessarily to be as high as possible [7]. For example, in PP used for biaxially oriented film (BOPP), presence of suitable amount of stereo defects in the PP chains will greatly influence its orientation behaviors, thus improve the performances and quality of the BOPP film. In this case, a combination of low amount of atactic fraction and medium number of stereo defects in the isotactic part will be the most favorable.

On the other hand, application of external donor usually causes remarkable increase of the polymer molecular weight, which leads to poor polymer processability. The sensitivity of the PP molecular weight to hydrogen, a chain transfer agent used in PP production, is lowered by introducing silane type external donor, especially when DCPDMS is used. This causes extra difficulties of regulating the PP molecular weight. To solve this problem, studies on new type of external donors are necessary.

In this work, the effects of two silane type external donors (Ph₂Si(OCH₃)₂ (DPDMS) and DCPDMS) on propylene polymerization with a MgCl₂/TiCl₄/DIBP catalyst were investigated, and the tacticity and molecular weight distributions of PP were further regulated by using silane-ether composite external donors. By using the composite external donors, PP with both higher isotacticity index and lower molecular weight was prepared, and the isotacticity distribution of PP was further changed based on the systems without ether. Effects of the external donors on the active center distribution are analyzed, and possible mechanism of the external donor effects is proposed.

**Results and Discussion**

*Influence of silane type donor on propylene polymerization*

Dicyclopentylidimethoxysilane (DCPDMS) or diphenylidimethoxysilane (DPDMS) was used as external electron donor (ED), respectively, in propylene polymerization. The
polymerization results are shown in Table 1. Comparing with the polymerization of propylene in the absence of external donor (Run PP-1), addition of DCPDMS or DPDMS caused an increase in catalytic activity and isotacticity index of PP. Furthermore, when DCPDMS was used as external donor, the catalytic activity, isotacticity index and molecular weight of PP were obviously higher than the system using DPDMS as external donor. These polymerization results were similar to the previous reports of other research groups [8, 9].

Tab. 1. Influences of silane external donor on propylene polymerization a.

<table>
<thead>
<tr>
<th>Sample</th>
<th>External donor</th>
<th>Si/Ti (mol/mol)</th>
<th>Activity (kg/g Ti·h)</th>
<th>I.I. b (%)</th>
<th>$M_w \times 10^{-4}$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP -1</td>
<td>none</td>
<td>0</td>
<td>29±2</td>
<td>64.7</td>
<td>7.5</td>
<td>6.1</td>
</tr>
<tr>
<td>PP -2</td>
<td>DPDMS</td>
<td>5</td>
<td>47±2</td>
<td>93.6</td>
<td>10.7</td>
<td>7.0</td>
</tr>
<tr>
<td>PP -3</td>
<td>DCPDMS</td>
<td>5</td>
<td>69±3</td>
<td>96.1</td>
<td>17.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>

a. Polymerization conditions: [Ti] = 0.1 mmol/L; AlEt$_3$/Ti = 200 (mol/mol); $T_p = 70^\circ$C; $t = 30$ min; $P_{Pr} = 3$ bar; $H_2/Pr = 0.05$;  

b. I.I. = isotacticity index.

Fig. 1. MWD curves (a) and their deconvolution into multiple Flory components (b, c and d) of PP prepared without external electron donor and with DPDMS or DCPDMS as external electron donor.
The multiplicity of active centers in MgCl₂-supported Z–N catalysts has been widely recognized. It has been proved that deconvolution of polymer MWD by multiple Flory functions [10,11] is an effective method to study the active center distribution of the catalyst. Figure 1-a shows the MWD curve of the PP samples (PP-1~3) of Table 1. The results of their deconvolution into six Flory “most-probable” distribution peaks are shown in Figure 1-b~d. MWD curves of the three samples were deconvoluted in the way described in our previous work [11]. It can be seen that the deconvolutions are quite accurate. The three samples were all deconvoluted into six Flory components. The six most probable peaks (the Flory components) were named as peaks A, B, C, D, E and F, respectively. A reasonable and straightforward explanation to this accurate deconvolution is that on the TiCl₄/MgCl₂/DIBP catalyst there exist six types of active centers that produce PP of different molecular weights. Based on this hypothesis, we can say that each Flory component corresponds to a certain type of active center, and there are six types of active centers, C*₁, C*₂, C*₃, C*₄, C*₅, and C*₆ in the catalysis systems. The abscissa value (representing the molecular weight of PP produced by the corresponding active center) and the area (representing the activity of the corresponding active center) of each peak were summarized in Figure 2-a and b, respectively. According to Figure 2-a, the molecular weight of PP produced by the six types of active centers increased in the order of: no ED < DDS < DCPDMS. According to Figure 2-b, the activities of all the active centers except C*₁ were enhanced by the external donor in the order of: no ED < DPDMS < DCPDMS. DCPDMS showed strong activation effect on the active centers C*₄, C*₅ and C*₆ that produce low molecular weight polymer, but the activity increment of C*₂ and C*₃ were relatively smaller. It is worthwhile to note that DCPDMS exerted deactivation effect on C*₁. The mechanism of the external effects will be discussed later in this paper.

The PP samples were respectively fractionated by boiling n-heptane into two parts, namely n-heptane-soluble part and n-heptane-insoluble part. The insoluble parts were characterized by DSC after being treated by successive self-nucleation and annealing (SSA). This SSA treatment is a kind of thermal fractionation that is widely applied in characterizing the chain structure of polyolefins [12]. In the SSA treatment, isotactic PP sequences with different lengths are allowed to crystallize at different temperatures to form crystalline lamella that melt at different temperatures. The thermogram of the SSA treated samples (as shown in Table 2 and Figure 3) can thus reflect the distribution of isotactic PP sequences [13]. According to Table 2, the
melting temperature and crystallinity of the n-heptane-insoluble part of PP synthesized using DCPDMS or DPDMS as external donor were higher than PP synthesized in the absence of external donor. Data from the conventional DSC analysis give the same trend, though with a lower distinguishing power. Furthermore, the melting temperature and crystallinity of the sample synthesized with DCPDMS was higher than that with DPDMS.

Tab. 2. Results of SSA and DSC analysis on PP prepared under different conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>External donor</th>
<th>SSA (\Delta H) (J/g)</th>
<th>(T_m) (ºC)</th>
<th>(X_c^b) (%)</th>
<th>DSC (\Delta H) (J/g)</th>
<th>(T_m) (ºC)</th>
<th>(X_c^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP -1</td>
<td>none</td>
<td>109.2</td>
<td>169.3</td>
<td>52.2</td>
<td>79.7</td>
<td>155.1</td>
<td>38.1</td>
</tr>
<tr>
<td>PP -2</td>
<td>DDS</td>
<td>122.8</td>
<td>170.5</td>
<td>58.8</td>
<td>90.3</td>
<td>160.2</td>
<td>43.2</td>
</tr>
<tr>
<td>PP -3</td>
<td>DCPDMS</td>
<td>127.7</td>
<td>176.2</td>
<td>61.1</td>
<td>91.5</td>
<td>161.6</td>
<td>43.8</td>
</tr>
</tbody>
</table>

a. Obtained from thermogram of samples treated by successive self-nucleation and annealing (SSA). b. Calculated based on the \(\Delta H\) of a perfectly crystalline PP of 209 J/g. c. Obtained from conventional DSC analysis.

Fig. 3. SSA thermograms of n-heptane insoluble fractions of PP.

As seen in Figure 3, on the SSA thermogram of PP prepared in the absence of external donor, there were several melting peaks at temperature lower than 165 ºC. These peaks should be originated from lamella formed by relatively short isotactic PP sequences. Its largest melting peak appeared at lower than 170 ºC. Using DPDMS as external donor led to increase in the PP's heat of fusion (\(\Delta H\)). Those peaks appeared at lower than 165 ºC became smaller, but a small peak appeared at about 175 ºC. This means that the amount of short isotactic PP sequences decreased, while the amount of long isotactic sequences increased after adding DPDMS in the polymerization system. Using DCPDMS as external donor, this trend became more evident. Now the melting peaks at 173~176 ºC become the main part of the endotherm. It is clear that adding external donor lead to improvement in isotacticty of all the PP chains in the n-heptane-insoluble fraction. This kind of donor effect can be
explained by a mechanistic model proposed by Busico V. et al [14]. In this model, the silane coordinates at catalyst surface in vicinity to the active site and increase its isospecificity. The bulky hydrocarbyl groups can protect the silane from leaving the catalyst surface via complexation with the alkylaluminium. Since the bulkiness of cyclopentyl group is larger than that of phenyl group, it is more difficult for the alkylaluminium to approach DCPDMS than to approach DPDMS. Therefore, complexation of DCPDMS by the alkylaluminium would be more difficult than that of DPDMS. As a result, using DCPDMS as external donor produced PP with higher isotactivity.

As to the effects of external donor on the activity of different active centers of the same catalyst, it seems that increasing the isospecificity of an active center is accompanied by increase in activity and decrease in chain transfer rate. This means that formation of stereodefects in the PP chain retards the chain propagation, because resuming isospecific propagation after a misinsertion would take longer time than a normal insertion step. Reduction of stereodefects can thus lead to higher activity. However, there is a clear exception to this law: the active center that produces PP of the highest molecular weight (C^*_A) was deactivated by addition of DCPDMS, a donor with very strong ability to improve stereospecificity. We guess that C^*_A has the most congested stereochemical environment among the six types of active centers, and this spacial congestion may become worse after the coordination of the donor molecules. Above a certain level of spacial congestion, coordination of the monomer on the active center may become hindered, leading to lowered activity.

Influence of DPDMS/ether composite external donor on propylene polymerization

To further regulate the chain structure of PP synthesized in the presence of silane type external donor, two ethers (ROCH_3, R = n-Bu or i-C_8H_17) were respectively mixed with DPDMS to form composite external donor for propylene polymerization. The polymerization results are summarized in Table 3. As shown in Table 3, using n-BuOCH_3 as an auxiliary external donor resulted in increase in catalytic activity. When the n-BuOCH_3/Ti molar ratio was 30, the catalytic activity could be increased by about 30%. However, using i-C_8H_17OCH_3 exerted no influence on the catalytic activity. Meanwhile, both n-BuOCH_3 and i-C_8H_17OCH_3 increased the polymer’s isotacticity. The molecular weight of PP was only slightly changed when either n-BuOCH_3 or i-C_8H_17OCH_3 was added as the auxiliary external donor. Judging from these results, it can be said that the effects of adding n-BuOCH_3 are quite beneficial, as it leads to the production of PP with higher isotacticity at higher activity.

To investigate the effects of ether addition on the active center distribution, the MWD curves of samples of Table 3 were deconvoluted into six Flory components, respectively. Figure 4-a and b show the molecular weight of PP produced by different active centers and the activity of the active centers resolved by the deconvolution, respectively. It can be seen that using n-BuOCH_3 as the auxiliary donor caused only slight increase in the molecular weight of PP produced by all the six active centers. However, the catalytic activities of C^*_D ~ C^*_F (especially C^*_D and C^*_E) that produce PP with lower molecular weight were increased by the addition of n-BuOCH_3. Meanwhile the catalytic activities of C^*_C ~ C^*_A which produce PP with higher molecular weight were more or less unchanged. This means that the active centers C^*_D, C^*_E and C^*_F were activated by the ether, while the active centers C^*_C, C^*_B and C^*_A were less influenced. Because the polymer’s isotacticity has also been improved by the ether, it
is likely that the stereospecificities of most of the active centers have also been increased by ether addition.

Tab. 3. Influence of DPDMS/ether composite external donor on propylene polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ether</th>
<th>Ether/Ti (mol/mol)</th>
<th>Activity (kg/gTi·h)</th>
<th>I.I. (%)</th>
<th>$M_n$ ($\times 10^4$)</th>
<th>$M_w/M_n$</th>
<th>$\Delta H^c$ (J/g)</th>
<th>$T_m^c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-2</td>
<td>none</td>
<td>0</td>
<td>47±2</td>
<td>93.6</td>
<td>10.7</td>
<td>7.0</td>
<td>90.3</td>
<td>160.2</td>
</tr>
<tr>
<td>PP-4</td>
<td>$n$-BuOCH$_3$</td>
<td>10</td>
<td>56±3</td>
<td>94.8</td>
<td>10.8</td>
<td>4.3</td>
<td>90.0</td>
<td>160.6</td>
</tr>
<tr>
<td>PP-5</td>
<td>$n$-BuOCH$_3$</td>
<td>20</td>
<td>54±3</td>
<td>95.5</td>
<td>11.9</td>
<td>4.9</td>
<td>90.2</td>
<td>160.9</td>
</tr>
<tr>
<td>PP-6</td>
<td>$n$-BuOCH$_3$</td>
<td>30</td>
<td>60±3</td>
<td>94.4</td>
<td>10.6</td>
<td>5.1</td>
<td>90.0</td>
<td>160.4</td>
</tr>
<tr>
<td>PP-7</td>
<td>$i$-C$<em>8$H$</em>{17}$OCH$_3$</td>
<td>10</td>
<td>47±2</td>
<td>94.1</td>
<td>12.6</td>
<td>4.3</td>
<td>89.1</td>
<td>160.8</td>
</tr>
<tr>
<td>PP-8</td>
<td>$i$-C$<em>8$H$</em>{17}$OCH$_3$</td>
<td>20</td>
<td>48±2</td>
<td>94.6</td>
<td>13.2</td>
<td>4.5</td>
<td>89.2</td>
<td>160.4</td>
</tr>
<tr>
<td>PP-9</td>
<td>$i$-C$<em>8$H$</em>{17}$OCH$_3$</td>
<td>30</td>
<td>47±2</td>
<td>94.3</td>
<td>11.3</td>
<td>4.4</td>
<td>91.4</td>
<td>160.6</td>
</tr>
</tbody>
</table>

*Polymerization conditions: [Ti] = 0.1 mmol/L, AlEt$_3$/Ti = 200 (mol/mol), DDS/Ti = 5 (mol/mol), $T_p$ = 70°C, $t$ = 30 min, $P_r$ = 2 bar, $H_2/Pr$ = 0.05, solvent = $n$-heptane; a I.I. = isotacticity index; c Thermal properties of the boiling $n$-heptane insoluble fractions determined by conventional DSC analysis.*

Fig. 4. Number average molecular weight (a) and activity (b) of the Flory components of PP prepared with DPDMS/$n$-BuOCH$_3$ composite external donor.

Deconvolution of the MWD curves of PP synthesized in the presence of DPDMS/$i$-C$_8$H$_{17}$OCH$_3$ composite external donor gave similar results. As shown in Figure 5, addition of $i$-C$_8$H$_{17}$OCH$_3$ lead to evident activation of the active centers $C_D^*$, $C_E^*$, and slight deactivation of $C_C^*$, $C_B^*$ and $C_A^*$.

Comparing to the SSA thermogram of PP synthesized without adding ether, an obvious change caused by adding either $n$-BuOCH$_3$ or $i$-C$_8$H$_{17}$OCH$_3$ as the auxiliary external donor is lowering of the melting peak appeared at 176 °C. It is found that the area percentage of the peak integration from 175 to 180 °C decreased from 7.6% of the system without ether addition to 2.6% and 4.6% of the DPDMS/$n$-BuOCH$_3$ ($n$-BuOCH$_3$/Ti = 30) and DPDMS/$i$-C$_8$H$_{17}$OCH$_3$ ($i$-C$_8$H$_{17}$OCH$_3$/Ti = 30) systems,
respectively. It indicates that using DPDMS/ether composite external donors could suppress the formation of PP chains with the highest isotacticity. On the other hand, the amount of PP segments with relatively lower isotacticity were slightly lowered by the addition of ether.

**Fig. 5.** Number average molecular weight (a) and activity (b) of the Flory components of PP prepared with DPDMS/i-C₈H₁₇OCH₃ composite external donors.

The chain structures of the n-heptane-insoluble parts of PP samples synthesized in the presence of DPDMS/ether composite external donors were characterized by SSA analysis, and the results are illustrated in Figure 6.

**Fig. 6.** SSA thermograms of boiling n-heptane insoluble fractions of PP prepared with DPDMS/n-BuOCH₃ (a) and DPDMS/i-C₈H₁₇OCH₃ (b) composite external donors.

For example, the half-height width of the main peak in the SSA thermogram was reduced from 7.2 °C of the system without ether to 6.4 °C of the DPDMS/ n-BuOCH₃ (n-BuOCH₃/Ti = 30) system, implying that the melting temperature of PP lamella was more concentrated to the range of 165-175 °C after ether addition. As a whole, the isotacticity distribution of PP can be markedly changed by adding n-BuOCH₃ or i-C₈H₁₇OCH₃ as auxiliary external donor. Such changes of isotacticity distribution could be beneficial to certain properties of PP. Reduction of PP chains or segments of the highest isotacticity (the SSA peak that has melting temperature higher than 175
°C) might help to reduce the formation of fisheye and form homogeneous crystalline structure in BOPP films.

To explain the above mentioned effects of adding ether as auxiliary external donor, the equilibria between the alkylaluminium and the two kinds of external donors (silane and ether) must be considered:

\[
\begin{align*}
\text{AlR}_3 & \iff \text{Silane} + \text{AlR}_3 \iff \text{Ether} - \text{Silane} - \text{Ether} \\
\text{AlR}_3 & \iff \text{Silane} + \text{Ether} - \text{Silane} - \text{Ether}
\end{align*}
\]

(1)

Our explanation for the effects of adding ether is: when a certain amount of ether is added into the polymerization system containing silane type external donor, a part of the alkylaluminium molecules will be coordinated by the ether, resulting in releasing of more free silane molecules. These silane molecules can thus coordinate with more active centers of low to medium isospecificity and turn them into isospecificity ones. This effect can explain the improvement in PP isotacticity by ether addition. On the other hand, though the monoethers studied in this work can only coordinate on the active centers weakly and thus cannot improve their isospecificity [15], they may temporarily replace the silane coordinated on the active centers, leading to temporary reduction of the active center's isospecificity. Such effects might be more serious on those active centers that have the highest isospecificity, because they have more congested space to ensure the coordination of the ether for enough long time before the ether is complexed by alkylaluminium. Therefore, number of stereoerrors in the PP chains produced by these active centers will be increased by addition of ether. This can explain the reduction of PP chains or segments of the highest isotacticity by the ethers.

**Influence of DCPDMS/ether composite external donor on propylene polymerization**

Although using DCPDMS as ED could produce PP with very high isotacticity, the molecular weight of PP was too high due to relatively low sensitivity of the catalyst to chain transfer with hydrogen. To overcome this shortage and regulate the chain structure of PP, the ether \(n\)-BuOCH\(_3\) was added together with DCPDMS to form composite external donor in propylene polymerization.

**Tab. 4. Influence of DCPDMS/ether composite external donor on propylene polymerization.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ether (mol/mol)</th>
<th>Activity (kg/gTi·h)</th>
<th>I.I. (^b) (%)</th>
<th>(M_w) (\times 10^{-4})</th>
<th>(M_w/M_n)</th>
<th>(\Delta H) (^c) (J/g)</th>
<th>(T_m) (^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-3</td>
<td>none</td>
<td>0</td>
<td>96.1</td>
<td>17.8</td>
<td>4.8</td>
<td>91.5</td>
<td>161.6</td>
</tr>
<tr>
<td>PP-10</td>
<td>(n)-BuOCH(_3)</td>
<td>10</td>
<td>95.8</td>
<td>19.4</td>
<td>5.0</td>
<td>91.2</td>
<td>162.6</td>
</tr>
<tr>
<td>PP-11</td>
<td>(n)-BuOCH(_3)</td>
<td>20</td>
<td>96.4</td>
<td>17.1</td>
<td>5.2</td>
<td>91.1</td>
<td>162.7</td>
</tr>
<tr>
<td>PP-12</td>
<td>(n)-BuOCH(_3)</td>
<td>30</td>
<td>97.5</td>
<td>15.6</td>
<td>5.0</td>
<td>92.3</td>
<td>162.4</td>
</tr>
</tbody>
</table>

\(^a\) Polymerization conditions: [Ti] = 0.1 mmol/L, AlEt\(_3\)/Ti = 200 (mol/mol), DCPDMS/Ti = 5 (mol/mol), \(T_p\) = 70°C, \(t = 30\) min, \(P_r\) = 2 bar, \(H_2/Pr = 0.05\), solvent = \(n\)-heptane; \(^b\) I.I. = isotacticity index. \(^c\) Thermal properties of the boiling \(n\)-heptane insoluble fractions determined by conventional DSC analysis.
As the polymerization results shown in Table 4, using \( n\)-BuOCH\(_3\) as auxiliary external donor resulted in increase of catalytic activity. Meanwhile, adding the ether slightly increased the isotacticity index of PP. Another effect of adding \( n\)-BuOCH\(_3\) is lowering of PP’s molecular weight. When the ether/Ti molar ratio was 30, the molecular weight decreased by about 10%. The melting temperature and heat of fusion of PP did not change much when \( n\)-BuOCH\(_3\) was used as auxiliary external donor.

The MWD curves of PP synthesized in the presence of DPDMS/\( n\)-BuOCH\(_3\) composite external donors were also deconvoluted into six Flory components, respectively, and the results are shown in Figures 7-a and b, respectively. It is seen that the molecular weight of PP produced by all the six active centers decreased as the amount of \( n\)-BuOCH\(_3\) increased. According to Figure 4-b, the catalytic activity of \( C_D \sim C_F \) that produce PP with lower molecular weight decreased as the amount of \( n\)-BuOCH\(_3\) increased. Meanwhile, the activity of \( C_C \) which produced PP with medium molecular weight did not change much. However, the catalytic activity of \( C_A \) and \( C_B \) which produced PP with higher molecular weight increased. Therefore, \( n\)-BuOCH\(_3\) tends to suppress the activity of \( C_D \sim C_F \) but enhance the activity of \( C_A \) and \( C_B \).

![Fig. 7. Number average molecular weight (a) and activity (b) of the Flory components of PP prepared with DCPDMS/\( n\)-BuOCH\(_3\) composite external donors.](image)

The \( n\)-heptane-insoluble parts of PP samples synthesized in the presence of DPDMS/\( n\)-BuOCH\(_3\) composite external donors were characterized by SSA thermo analysis, and the results are illustrated in Figure 8. As compared to the sample prepared without ether addition, only slight changes in the thermograms were caused by adding \( n\)-BuOCH\(_3\) in the polymerization system. When we look into the details of these thermograms, it is found that the shoulder peak at 173 °C of the sample without ether became the main peak in the sample of ether/Ti = 30, and the 176.5 peak was shifted to about 175.5 peak after adding the ether. Therefore, addition of the ether as the auxiliary external donor made only minor regulation on the isotacticity distribution. The regulation effects are similar to those observed in the systems of DPDMS/ether composite external donor, namely, the PP chains or segments with the highest isotacticity (peak higher than 175 °C) and those with low to medium isotacticity (shoulder peaks at and lower than 171 °C) are reduced by the ether, while the PP fractions with the second highest isotacticity (peak at 173 -173.5 °C) are increased, though not so evident as in the systems with DPDMS/ether composite external donor. The effects of adding ether in a MgCl\(_2\)/TiCl\(_4\)/DIBP-TEA/DCPDMS catalyst system are weaker than the system containing DPDMS as the main external donor. The reason
for this difference may lie in the fact that DCPDMS can coordinate on the active centers more firmly than DPDMS, owing to the larger steric hindrance in the former silane to the complexation of alkylaluminium molecules. More experimental evidences are to be collected to give a more reasonable explanation to the effects of composite external donors on propylene polymerization.

Fig. 8. SSA thermograms of boiling n-heptane insoluble fractions of PP prepared with DCPDMS/n-BuOCH₃ composite external donors.

Conclusions
In conclusion, addition of dicyclopentyl(dimethoxysilane (DCPDMS) or diphenyl(dimethoxysilane (DPDMS) to MgCl₂/TiCl₄/DIBP-TEA catalyst system as external electron donor lead to increase in propylene polymerization activity as well as polymer’s isotacticity and molecular weight. The isotacticty distribution of PP, as revealed by SSA thermo analysis of the polymer, is also markedly changed by the donors. DCPDMS shows much stronger effects than DPDMS. Addition of ether (ROCH₃, R = n-Bu or i-C₈H₁₇) as auxiliary external donors in propylene polymerization with MgCl₂/TiCl₄/DIBP-TEA/silane (DPDMS or DCPDMS) lead to further increase in catalytic activity and isotacticity, and changes in isotacticy distribution. In comparison, adding ether in MgCl₂/TiCl₄/DIBP-TEA/DPDMS system caused more evident changes in isotacticty and its distribution, while adding n-BuOCH₃ in MgCl₂/TiCl₄/DIBP -TEA/DCPDMS system mainly caused decrease in molecular weight. Addition of ROCH₃ type monoethers as auxiliary external donors is an effective way of regulating the chain structure and molecular weight of PP without sacrificing the polymerization activity.

Experimental Part
Preparation of ethers
Two kinds of ether (ROCH₃, R = n-Bu or i-C₈H₁₇) were prepared according to the following reactions [16], respectively:
Yields of the reactions were about 80%. The ethers were purified by distillation to about 98% purity. $^1$H NMR (CDCl$_3$, 25 °C): $n$-BuOCH$_3$, $\delta$ = 0.90, 0.92, 0.95 (t, 3H), 1.31-1.43 (m, 2H), 3.33 (s, 3H); $i$-C$_8$H$_{17}$OCH$_3$, $\delta$ 0.91, 0.93 (d, 6H), 1.5-2.2 (m, 9H), 3.13, 3.15 (d, 2H), 3.35 (s, 3H). The ethers were then dried with 4A molecular sieve and diluted in n-heptane before use.

### Propylene polymerization

Propylene polymerization was carried out in a 1 L autoclave with mechanical stirrer and heating jacket. The reaction temperature was stabilized at 70 °C. The autoclave was evacuated and purged by 1 bar propylene (produced by Yangzi Petrochemical Co., Nanjing, China) for three times, and then filled with 300 mL n-heptane. 1 M n-heptane solution of the cocatalyst Al(C$_2$H$_5$)$_3$ (TEA, purchased from Albermarle Co.) and the external donor were added in that order. As the external donors used in this work, Ph$_2$Si(OCH$_3$)$_2$ (DPDMS) and (cyclo-C$_5$H$_9$)$_2$Si(OCH$_3$)$_2$ (DCPDMS) were purchased from Hubei Huabang Chemicals, Co., Hubei, China, and distilled before use. 50 mL H$_2$ was then added into the autoclave. Finally, about 60 mg MgCl$_2$/TiCl$_4$/DIBP catalyst (kindly donated by Yangzi Petrochemical Co., Nanjing, China) was added into the autoclave, and the propylene pressure was raised to 3 bar to start the polymerization. Then propylene at 3 bar was continuously supplied into the autoclave to maintain a constant pressure. After 30 min, the pressure was released and the polymerization slurry was poured into 500 ml ethanol containing 2 ml hydrochloric acid to terminate the reaction and settling down the polymer. The polymer particles were filtered and then washed with ethanol and vacuum dried at 60 °C. The polymerization activity data were reproducible with an average error of ±5% according to repeated experiment runs.

The isotacticity index of the synthesized polypropylene was measured by extracting about 1 g polypropylene sample with boiling n-heptane in a Kumagawa extractor for 12 h. The details of the measurement are as follows: the polypropylene sample was first weighed in an analytical balance with ±0.1 mg accuracy, loosely wrapped in a piece of filter paper, and put into the extraction chamber of the Kumagawa extractor. 200 ml n-heptane was poured into the extractor, and heated to boiling with a heating mantle for 12 h. After ceasing the heating, the pack of filter paper containing the insoluble polymer was taken out and dried in a vacuum oven at 60 °C and 2 mmHg for 8 h. The insoluble polymer was weighed in the same balance, and the weight percentage of insoluble part in the original sample was taken as the isotacticity index (I.I.). From the results of parallel extraction experiments of the same sample, it was found that the average deviation of I.I. (%) determined in this way was ±0.1%.

### Polymer characterization

Molecular weight and molecular weight distribution (MWD) of the PP samples were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories Ltd.) at 150 °C in 1,2,4-trichlorobenzene. Three PL mixed B columns (500–10$^7$) were used. Universal calibration against narrow polystyrene standards was adopted.
Successive self-nucleation and annealing (SSA) measurement of the synthesized PP samples was made with a TA Instruments Q200 differential scanning calorimeter in a nitrogen atmosphere. About 4 mg polymer sample was sealed in aluminium pan for the measurement. The procedures of SSA measurement were similar to the original literatures of the field [12, 13]. The annealing time was kept at 5 min. The thermal history of the samples was first erased by heating to 210 °C and keeping for 5 min. The first annealing temperature \( T_0 \) was fixed at 170 °C for all the samples, and the succeeding annealing temperatures were 165, 160, 155, 150, 145, 140, 135, and 135 °C, respectively. Heating and cooling were done at a rate of 10 °C/min. The crystallinity was calculated by comparison with heat of fusion (\( \Delta H_f \)) of a perfectly crystalline polypropylene, i.e. 209 J/g [17].

Conventional DSC analysis of the PP samples were made with a TA Instruments Q200 differential scanning calorimeter in a nitrogen atmosphere. The samples were first heated to 190 ºC and kept for 5 min to eliminate thermal history, and then cooled to room temperature at 10 ºC /min. The second heating scan at 10 ºC /min was recorded.

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References