ABSTRACT

Two different monoethers, CH₃CH₂CH₂CH₂OCH₃ (NBME) and (CH₃)₂CHCH₂-OCH₃ (IBME), and Ph₂Si(OCH₃)₂ were used as external donors in propylene polymerization using MgCl₂/TiCl₄/DIBP catalyst (DIBP: diisobutyl phthalate) activated by triethylaluminium (TEA). The monoethers alone showed no improvement in the isotacticity index of polypropylene (PP). When one of the ethers and Ph₂Si(OCH₃)₂ were added together in the polymerization system as composite external donors, the propylene polymerization activity and isotacticity index were increased as compared to those of the systems with only silane as external donor, though the melting temperature and melting enthalpy of PP decreased. The effects of the external donors on the active center distribution of the catalyst system are demonstrated by deconvolution analysis of the PP molecular weight distribution into multiple Flory components, and the mechanism of external donor regulation effects is discussed. All the results show that adding monoether in MgCl₂/TiCl₄/DIBP-TEA/silane catalyst system can reduce the stereoregularity of the isotactic chains of the polymer while, it maintains the atactic PP fractions at a very low level.

INTRODUCTION

High-activity TiCl₄/MgCl₂/ID type (ID: internal donor) Ziegler-Natta catalysts play a dominant role in the industrial production of isotactic polypropylene (PP). In this type of catalyst, the most widely used internal donors are dialkyl phthalates, such as diisobutyl phthalate (DIBP) [1]. The so called "external" electron donors (ED) are also added in the polymerization system together with the co-catalyst triethyl aluminium (TEA). The main role of the external donor is to improve the isotacticity of PP. 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, among which alkoxy-silanes are found to be best compared to other types of external donor in relation to isotacticity and polymerization activity [2-5].

However, the so-called isotacticity index (I.I.) which is the
fraction of insoluble PP in cold xylene or boiling n-heptane can just roughly reflect the chain structure of PP. In fact, when the PP sample is fractionated by "temperature rising elution fractionation", a very broad distribution of fractions can be observed [6,7]. These fractions eluted at different temperatures show different degrees of crystallinities, which are determined by the amount of stereo-defects in the PP chains. This means that PP synthesized with supported Ziegler-Natta catalysts is composed of a series of chains with different stereoregularities and the isotacticity index only reflects the total amount of PP chains with medium to high isotacticity.

In the studies of external donor effects, information of the chain structure distributions is even more important than the isotacticity index. As reported by Chadwick et al. [2,8] changing the external donor from cyclohexyl(methyl)dimethoxysilane to dicyclopentyldimethoxysilane in propylene polymerization with MgCl₂/TiCl₄/DIBP catalyst not only the polymer's isotacticity index increases, but also a remarkable shift of the "temperature rising elution fractionation" peak to the high temperature end takes place. This means that enhancing PP isotacticity by using alkoxyasilane 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 unfavourable limitation to modification of PP properties by application of external donors, because the properties of PP is not only determined by its atactic fraction (i.e., the fraction soluble in cold xylene or boiling n-heptane), but more dominantly, by the entire tacticity distribution. For this reason, it is necessary to find new types of external donors that can improve not only the isotacticity of PP, but also its 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 of PP. Reducing this fraction in PP is usually favourable. However, the stereoregularity of the "isotactic" fractions which determine the crystallinity of PP and therefore its physical properties is not necessary to be very much high. For example, in PP used for biaxially oriented film (BOPP), presence of suitable amounts of stereo-defects in PP chains will greatly influence its orientation behaviour, thus improves the performances and quality of the BOPP films [9,10]. In this case, a combination of low percentage of atactic fractions and moderate amounts of stereo-defects in the isotactic fractions would be the most favourable conditions.

In this work, the effects of ROCH₃ type monoethers as external donors on propylene polymerization with a MgCl₂/TiCl₄/DIBP catalyst were investigated, and composite external donor ethers and Ph₂Si(OC₃H₇)₂ were used to regulate the tacticity distribution of PP. By using the composite external donors, PP was prepared with high isotacticity index and lower melting temperature and crystallinity content. Such effects of silane/ether composite donors have not been reported in literature before. This kind of composite external donors may be used in the synthesis of isotactic PP with lower melting temperature to meet the needs of some special applications. The possible mechanism of the regulation effects of the composite donors is offered and discussed in this work.

EXPERIMENTAL

Materials
Two different ethers, CH₃CH₂CH₂CH₂OCH₃ (NBME) and (CH₃)₂CHCH₂OCH₃ (IBME) were prepared by reactions of CH₃ONa with n-butyl chloride and i-butyl bromide, respectively [11]. Yield of the reactions was about 80%. The ethers were purified by distillation to about 98% purity.

1H NMR (CDCl₃, 25°C): n-BuOCH₃, δ = 0.90, 0.92, 0.95 (t, 3H), 1.31-1.43 (m, 2H), 1.51-1.61 (m, 2H), 3.33 (s, 3H), and 3.35, 3.38, 3.40 (t, 2H); i-BuOCH₃, δ = 0.89, 0.92 (d, 6H), 1.77-1.91 (m, 1H), 3.11, 3.13 (d, 2H), and 3.31 (s, 3H).

Propylene Polymerization
A 100-mL Schlenk bottle, while immersed in a 50°C oil-bath, was evacuated and purged by nitrogen three times and then filled with propylene at 1 atm. A volume of 50 mL n-heptane as solvent, a definite volume of co-catalyst (Al(C₂H₅)₃ (TEA, purchased...
from Albermarle Co. and diluted in \textit{n}-heptane before use)) and external donors (\textit{n}-BuOCH\textsubscript{3}, \textit{i}-BuOCH\textsubscript{3}, \textit{Ph}_{2}\text{Si(OCH}_{3})_{2} (DPDMS, purchased from Hubei Huabang Chemicals, Co., Hubei, China), or mixtures of ether with DPDMS) in \textit{n}-heptane were added in the above order under stirring. A sample of 40-50 mg MgCl\textsubscript{2}/TiCl\textsubscript{4}/DIBP catalyst (Ti content 2.7%, kindly donated by Yangzi Petrochemical Co., Nanjing, China) was added into the flask after 1 min to start the polymerization. Polymerization grade propylene (produced by Yangzi Petrochemical Co., Nanjing, China) at 1 atm was continuously supplied into the flask to maintain a constant pressure. After 30 min, propylene inlet was stopped and the polymerization slurry was poured into 200 mL ethanol containing 1 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 isotacticity index of the synthesized polypropylene was measured by extracting about 1 g sample with boiling \textit{n}-heptane in a Kumagawa extractor for 12 h, and the weight percentage of insoluble part was taken as the isotacticity index (I.I.).

**Polymer Characterization**

The molecular weight and molecular weight distribution (MWD) of the PP samples were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories Ltd., UK) at 150°C in 1,2,4-trichlorobenzene. Three PL mixed B columns (500-10\textsuperscript{7}) were used. A universal calibration against narrow polystyrene standards was adopted.

Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 (USA) thermal analyzer. The polymer sample (about 4 mg) was sealed in aluminium pan, which was then sealed in a glass tube under nitrogen atmosphere. The glass tubes were immersed in an oil bath and heated to 180°C, kept at that temperature for 30 min, and annealed at 140°C, 130°C, 120°C, 110°C, 100°C, 90°C, 80°C, 70°C, 60°C, and 50°C, respectively, each for 12 h. The treated samples were then scanned in DSC from 50 to 180°C at a heating rate of 10°C/min. Both the boiling \textit{n}-heptane soluble and insoluble fractions were collected for the DSC analysis.

**RESULTS AND DISCUSSION**

**Effects of Single Ether as an External Donor**

Two kinds of monoethers, NBME and IBME, were used as external donors in propylene polymerization with the catalyst system MgCl\textsubscript{2}/TiCl\textsubscript{4}/DIBP-TEA. Propylene polymerizations were run under the same conditions without any external donor and in presence of DPDMS as external donor for comparison. Figure 1 shows the polymerization activity. It is evident that by adding any of the ethers or DPDMS would reduce activity slightly, and there are only small changes in activity when the ether/Ti molar ratio increased from 5 to 20. The isotacticity index and data of GPC analysis of the samples in Figure 1 are listed in Table 1.

In Table 1 we can see that the isotacticity index of the PP synthesized in the presence of NBME or IBME are almost the same as the sample prepared without using the external donor. This is in sharp contrast to a rather high isotacticity index of the PP prepared using DPDMS as external donor. This means that by applying the ether alone as external donor, it is not possible to improve the stereoregulation ability of the catalyst. On the other hand, weight average molecular weights of the samples in Table 1 are similar to each other.

To characterize the distribution of tacticity in the PP samples, both the boiling \textit{n}-heptane soluble
fraction and the insoluble fraction of the PP were analyzed by DSC thermal analysis. As described in the experimental part, samples for DSC analysis were annealed in a stepwise mode at a series of temperatures to allow the isotactic chain segments crystallize and form crystalline lamella with different melting temperatures [12]. This kind of treatment is called "thermal fractionation", which is widely applied in characterizing the chain structure of polyolefins. The DSC thermogram of the stepwise annealed samples can thus reflect the distribution of isotactic sequences [13]. Figures 2 and 3 present the DSC thermograms of the boiling n-heptane insoluble and soluble fractions, respectively. The data of melting temperature and melting enthalpy are listed in Table 1.

As shown in Figure 2 and Table 1, the insoluble fraction of PP synthesized in the presence of NBME or IBME have similar melting temperatures as that of the sample of an external donor free system. The melting enthalpies of the formers are even slightly smaller than that of the latter. The range of melting peaks are also similar with each other. This means that addition of ether caused little changes in the tacticity distribution of PP chains of high stereoregularity. In contrast, using DPDMS as an external donor led to a marked increase of melting temperature and melting enthalpy of the insoluble fraction.

As to the boiling n-heptane soluble fraction, DSC thermograms with multiple melting peaks were observed for all the four samples in Table 1 (Figure 3). The peaks located at high temperature range represent longer crystallizable PP segments, or PP chains with higher isotacticity, as they form thicker crystalline lamella that melt at higher temperature.

### Table 1. Influences of external donors on propylene polymerization.

<table>
<thead>
<tr>
<th>Run</th>
<th>External donor</th>
<th>ED/Ti (kg PP/g Ti-h)</th>
<th>Activity (kg PP/g Ti-h)</th>
<th>I.I. (%)</th>
<th>Mw (x 10^-4)</th>
<th>PDI</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>none</td>
<td>0</td>
<td>5.0</td>
<td>65.8</td>
<td>11.6</td>
<td>13.1</td>
<td>160.4</td>
<td>87.0</td>
<td>11.6</td>
</tr>
<tr>
<td>P-2</td>
<td>DPDMS</td>
<td>5</td>
<td>3.6</td>
<td>94.8</td>
<td>11.7</td>
<td>8.7</td>
<td>165.1</td>
<td>104.4</td>
<td>31.0</td>
</tr>
<tr>
<td>P-5</td>
<td>NBME</td>
<td>20</td>
<td>3.6</td>
<td>67.4</td>
<td>11.9</td>
<td>14.1</td>
<td>158.8</td>
<td>80.4</td>
<td>16.7</td>
</tr>
<tr>
<td>P-11</td>
<td>IBME</td>
<td>20</td>
<td>4.0</td>
<td>66.6</td>
<td>11.0</td>
<td>9.4</td>
<td>160.5</td>
<td>81.6</td>
<td>19.3</td>
</tr>
</tbody>
</table>

(a) Catalyst: MgCl2/DIBP/TiCl4; cocatalyst: TEA; polymerization conditions: [Ti] = 0.5 mmol/L; Al/Ti = 100 (mol/mol); Tp = 60°C; t p = 30 min; propylene pressure = 1 bar; solvent: n-heptane; (b) Isotacticity index expressed as percentage of boiling n-heptane insoluble fraction; (c) Molecular weight (Mw) and polydispersity index (PDI) determined by GPC; (d) Melting temperature (Tm) and melting enthalpy (ΔHm) of the boiling n-heptane insoluble fraction; (e) Melting enthalpy of the boiling n-heptane soluble fraction.
On this basis, it is clear that the n-heptane soluble fraction of PP synthesized without external donor has the lowest content of crystallizable PP segments. Addition of the ethers caused clear increase in crystallizable PP segments, especially those with high isotacticity, as the peaks in range of 120°C-160°C were enhanced more than those in the lower temperature. Therefore, we can conclude that at least a part of the active centres in the catalyst system is affected by adding the ether as external donor. A stronger effect of silane type external donor on the chain structure of boiling n-heptane soluble fraction can also be observed. As shown in Figure 3, adding DPDMS caused sharp increase of the peaks at high temperature range, especially the peak at 147°C, and the melting enthalpy was markedly increased.

**Influence of Ether on the Active Centre Distribution**

The multiplicity of active centres in TiCl₄/MgCl₂/ID type supported Z-N catalysts has become widely recognized [14-16]. It has been proved that deconvolution of polymer MWD by multiple Flory functions [16-18] is an effective method to study the active centre distribution of the catalyst. Figure 4 shows the MWD curve of the PP sample P-1 in Table 1 and the results of its deconvolution into six Flory "most-probable" distribution peaks. The deconvolution is quite accurate. MWD curves of the four samples in Table 1 were deconvoluted in the same way described in our previous work [16]. All the four samples were deconvoluted into six Flory components, respectively. Each Flory component corresponds to a certain type of active centre, thus there are six types of active centres, Cₐ, Cₑ, Cₖ, Cₜ, Cₜ, and Cₚ in the catalysis systems. Figure 5a shows the number average molecular weight of the Flory components, which reflects the frequency of chain transfer reaction of the active centres. Figure 5b shows the polymerization activity of the Flory components, which are calculated by multiplying the total polymerization activity by the fraction of each component.

In Figure 5 we can find that both the molecular
weight and activity of the Flory components are evidently changed by the addition of an external donor. Similar changes in MWD of PP caused by external donor have also been reported in literature [19]. Here, it may be seen that adding ethers would tend to decrease the molecular weight of all the components, but DPDMS only reduces the molecular weight of C*A, C*B and C*C. The changes made by the external donors on the distribution of activity, which is the most important feature of the active centre distribution, is even more evident. The three donors all caused sharp deactivation of the active centres that produce PP with low to medium molecular weights (C*C, C*D, C*E, and C*F), but the active centres producing high molecular weight PP (C*A and C*B) are slightly activated. Comparing with DPDMS, the effects of the two different ethers on the active centre distribution are relatively weaker.

Judging from these results of MWD deconvolution, we can say that the effects of ether type external donor are quite similar to the silane type donors, though the former shows rather weak ability to improve the active centre's stereospecificity.

Effects of Ether/Silane Composite External Donors

To explore the possibility of regulating the PP chain structure in a broader range, mixtures of NBME or IBME with DPDMS were used as external donors in the propylene polymerization, and the results are listed in Table 2.

It can be seen that adding ether (ether/Ti molar ratio = 20) along with silane does interfere with catalyst activity and isotacticity of PP. The activity and isotacticity are even slightly increased by adding IBME. On the other hand, the melting temperature and melting enthalpy of PP prepared with the composite external donors are still lower than the polymer prepared with a single DPDMS donor.

As shown in Figures 6 and 7, the DSC curves of the n-heptane insoluble and soluble fractions of PP prepared with the composite donors are quite different from those of the system with a single silane donor. Addition of the ether caused marked reductions in the melting temperature of insoluble fraction and melting enthalpy of the soluble fraction. Though, the polymerization activity and PP isotacticity are almost unchanged by adding the ether, the chain structure of PP is clearly changed. Such a change in chain structure of PP may be helpful for its better performance in applications like biaxially oriented films, as the isotacticity index is still rather high,

![Figure 6. DSC Curves of the boiling n-heptane insoluble part of the PP samples in Table 2.](image)

Table 2. Influences of silane/ether composite external donors on propylene polymerization a.

<table>
<thead>
<tr>
<th>Run</th>
<th>External donor</th>
<th>Ether/Ti</th>
<th>Activity (kg PP/g Ti·h)</th>
<th>I.I. b (%)</th>
<th>PDI c</th>
<th>$\bar{M}_w$ (× 10^{-4})</th>
<th>$\Delta H_m$ insol f J/g</th>
<th>$\Delta H_m$ sol f J/g</th>
<th>$T_m$ insol d °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2</td>
<td>DPDMS</td>
<td>0</td>
<td>3.6</td>
<td>94.8</td>
<td>11.7</td>
<td>8.7</td>
<td>165.1</td>
<td>104.4</td>
<td>31.0</td>
</tr>
<tr>
<td>P-14</td>
<td>DPDMS/NBME</td>
<td>20</td>
<td>3.6</td>
<td>95.0</td>
<td>12.3</td>
<td>8.2</td>
<td>161.2</td>
<td>95.4</td>
<td>26.4</td>
</tr>
<tr>
<td>P-20</td>
<td>DPDMS/IBME</td>
<td>20</td>
<td>4.4</td>
<td>95.8</td>
<td>12.8</td>
<td>10.2</td>
<td>161.8</td>
<td>102.6</td>
<td>13.1</td>
</tr>
</tbody>
</table>

(a) Catalyst: MgCl2/DIBP/TiCl4; cocatalyst: TEA; polymerization conditions: [Ti] = 0.5 mmol/L; Al/Ti = 100 (mol/mol); $T_p$ = 60°C; $t_p$ = 30 min; propylene pressure = 1 bar; solvent: n-heptane; DPDMS/Ti = 5 (mol/mol); (b) Isotacticity index expressed as percentage of boiling n-heptane insoluble fraction; (c) Molecular weight ($\bar{M}_w$) and polydispersity index (PDI) determined by GPC; (d) Melting temperature ($T_m$) and melting enthalpy ($\Delta H_m$) of the boiling n-heptane insoluble fraction; (e) Melting enthalpy of the boiling n-heptane soluble fraction.
while the crystallinity is decreased.

The active centre distributions of the polymerization systems with composite external donors are analyzed by deconvolution of the MWD curves by multiple Flory components, and the results are shown in Figure 8. In the presence of ether/silane composite donors, the MWD curves can still be deconvoluted into six Flory components. Addition of ether besides the silane brought about only slight changes in the molecular weight of the Flory components, but the distribution of activity was undoubtedly changed. With the use of IBME/DPDMS or NBME/DPDMS composite external donors, the activity of active centres producing PP of medium molecular weight (C* C, C* D, C* E, and C* B) was raised, while the activity of C* A and C* F was almost unchanged. This is consistent with the changes in the PP chain structure. By characterizing the chain structure of TREF fractions of PP synthesized with heterogeneous Ziegler-Natta catalyst, it has been found that the isotacticity of PP fraction is directly proportional to its molecular weight [20,21]. Namely, PP produced by C* C, C* D, C* E, and C* B centres have higher isotacticity than PP produced by C* F, and still lower isotacticity than that produced by C* A centre. Therefore, we can say that adding IBME or NBME to the MgCl₂/TiCl₄/DIBP-TEA/DPDMS catalyst system resulted in selective activation of the active centres with medium stereospecificity.

By comparing the behaviour of single ether type external donor and ether/silane composite external donors, a tentative mechanistic model can be proposed to explain the experiment phenomena observed in this work. At first, the main effects of the external donor in the polymerization can be depicted with the model proposed by Busico et al. [22]. In this model, the reversible coordination of the external donor on the Mg atoms adjacent to Ti atoms of the active centres increases its stereospecificity (Scheme I). On the other hand, an external donor can also coordinate to AlR₃ in the system, leading to lower concentration of free donor that can coordinate to the active centres (Scheme I). For external donors with only one coordinating atom, like monoethers,
the coordination is relatively weak. This leads to active centres with low isospecificity, because the equilibria between the active centre and external donor are shifted to the left side. For external donors with two methoxy groups, like \( R_2Si(OCH_3)_2 \), their coordination on the active centres would be much more stable, and great improvement of stereospecificity is achieved. When the monoether and silane type external donor are added together, the silane will play the dominant role in coordinating with the active centres to enhance their stereospecificity. The ether, though has lower coordination ability, can still compete with the silane in the reversible coordinations with \( AlR_3 \) and the active centres. The former competition leads to increased concentration of free silane, and thus increased isotacticity of PP. The latter competition, however, would moderately reduce the stereospecificity, as the ether with lower bulkiness is not so efficient in regulating the stereospecificity as the silane donor. Therefore, adding monoether in the \( MgCl_2/TiCl_4/DIBP-TEA \) catalyzed propylene polymerization. When ether/\( Ph_2Si(OCH_3)_2 \) composite external donors are added in the same catalyst system, the propylene polymerization activity and the isotacticity index (content of boiling \( n \)-heptane insoluble fraction) of PP are increased as compared to those of the systems with silane as the only external donor, and still the melting temperature and melting enthalpy of PP are lowered. Adding a suitable amount of monoether in \( MgCl_2/TiCl_4/DIBP-TEA/silane \) catalyst system serves as an effective way to reduce the stereoregularity of the isotactic chains in the polymer, meanwhile it keeps the atactic PP fractions at a very low level.

The active centre distributions of the polymerization systems are analyzed by deconvolution of the MWD curves by multiple Flory components. Comparing to the catalyst system with DPDMS as the only external donor, use of IBME/DPDMS or NBME/DPDMS composite external donors raises the activity of active centres producing PP of medium molecular weight more compared to other types of active centres.

**ACKNOWLEDGEMENT**

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