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Application of successive self-nucleation and annealing (SSA) to poly(1-butene) prepared by Ziegler-Natta catalysts with different external donors

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Alkoxy silane compounds R₁R₂Si(OMe)₂ were used as an external donor for 1-butene polymerization with MgCl₂ supported Ziegler-Natta catalysts. The structure of the prepared iPb was characterized by ¹³C NMR and GPC. The thermal property of poly(1-butene) (iPB) was studied by DSC. The crystallization behavior and the sequence length distribution of poly(1-butene) were investigated through the successive self-nucleation and annealing (SSA) thermal fractionation technology. The SSA results indicated that the steric hindrance of external donor has more influence on the property of iPb, the each peak of the melting point and the enthalpy of fusion of iPb gradually increased with the increase of steric hindrance of external donor. And considering all properties, cyclopentyl isopropyl dimethoxysilane had better advantage relative to other external donors in the polymerization of 1-butene.

Introduction

The isotactic poly(1-butene) (iPB) showed interesting physical and mechanical properties, such as heat-resistant creep degeneration, good environmental stress cracking resistance performance, and good tenacity. Therefore, the iPb could be used as pipe, film and sheet material, and especially as hot water pipe material. The isotactic poly(1-butene) was first synthesized by Ziegler-Natta catalysts. Although the catalyst used for preparing PE and PP was similar to that of iPb, the polymerization technology of 1-butene was difficult to implement which leads to higher cost and limits its commercial development. Isotactic poly(1-butene) was first synthesized by Ziegler-Natta catalysts. Although the catalyst used for preparing PE and PP was similar to that of iPb, the polymerization technology of 1-butene was difficult to implement which leads to higher cost and limits its commercial development. Isotactic polymer with higher degree of isotacticy and the desired physic-chemical properties of the product. In recent years, researchers had much concern for alkoxy silane as external donor of Ziegler-Natta catalyst. External donor had more influence on the microstructure of polypropylene. Busico et al. proposed a three-site model to explain the effects of external donor on catalyst efficiency and polypropylene stereoregularity. In this model, successive adsorption of D₆ on catalyst changed the stereochemical environment of the active center, which could turn atactic centers into isotactic centers. This model could also apply to other polyolefin.

Successive self-nucleation and annealing (SSA) was regarded as an effective technique to characterize the microstructure of polypropylene. Our research group had studied isotactic sequence length and its distribution of PP prepared by Ziegler Natta catalyst using different alkoxy silanes as external donor using SSA, which could be connected with many macro-properties, such as mechanic, thermal and process properties. Although there were many reports for the influence of external donor on propylene polymerization and polypropylene, the investigation of the effect of external donor on 1-butene polymerization and poly(1-butene) was few. Kudinova et al. reported the use of polydentate phosphine oxides as electro donor of TiCl₄-MgCl₂ catalysts could obtain highly isotactic poly(1-butene) and the isotactic index could reach 92.4% when the external donor was iso-AmP(O)(CH₂OMe)₂. Hegang Ren et al. studied diphényl dimethoxysilane or cyclohexyl methyl dimethoxysilane as external donor of TiCl₄-MgCl₂ catalysts, which external donor could improve the catalytic activity slightly and sharply increased the isotactic index, and cyclohexyl methyl dimethoxysilane has been found to be more effective electron donor than diphényl dimethoxysilane.

In this paper, poly(1-butene)s were prepared by Ziegler-Natta catalyst with different external donors. The effects of external donor on the molecular weight, the molecular weight distribution and isotactic index of poly(1-butene) were investigated, especially, SSA technique was first used for studying the microstructure and properties of poly(1-butene).

Experimental

Materials

MgCl₂-supported Ziegler-Natta catalyst (SAL, Ti content of 2.5%), triethyl aluminum (TEA) and 1-butene (polymerization grade) were provided by YanShan Petrochemical Co. Ltd. Cyclohexylmethyldimethoxysilane (Donor-C), Diisopropyl Dimethoxysilane (Donor-P), Diisopropyl Dimethoxysilane (Donor-D), Dicyclohexyl Dimethoxysilane (Donor-H) and
Cyclopentyltrimethoxysilane (CPTMS) were provided by LuJing Chemical. Isobutylmethyl Dimethoxysilane (Donor-MB), Isopropylmethyl Dimethoxysilane (Donor-MP), Cyclopentylmethyl Dimethoxysilane (Donor-MD), Isobutylisopropyl Dimethoxysilane (Donor-PB) and Cyclopentyl isopropyl Dimethoxysilane (Donor-PD) (Figure 1) were synthesized by our group.

Polymerization of 1-Butene

In a typical experiment, a 5L stainless reactor equipped with a mechanical stirrer was degassed at 70°C, and then the Ziegler-Natta catalyst (15mg), TEA (7.92mmol) in n-hexane solution and the alkoxy silane compounds (Si/Ti=20) were added. Then exclude unreacted 1-butene, subsequently, dried under vacuum at (Bruker). Polymer solution was prepared with 80mg of polymer using 1,2,4-trichlorobenzene as solvent, and the flow rate was 220 ml/min at 413K, high-temperature gel permeation chromatography at 413K, Isotacticity of the polymer obtained was determined by extracting sample.

Measurement

13C NMR spectra of polymers were recorded with a DMX 300M (Bruker). Polymer solution was prepared with 80mg of polymer in 0.5ml deuterated o-dichlorobenzene at 373K. The molecular weights ($M_\text{n}$ and $M_\text{w}$) and the molecular weight distribution (MWD) of samples were determined by a PL-GPC 220 high-temperature gel permeation chromatography at 413K, using 1,2,4-trichlorobenzene as solvent, and the flow rate was 1.0ml min$^{-1}$. Calibration was made by polystyrene as the standard sample.

Isotacticity of the polymer obtained was determined by extracting the polymer with boiling ether in a Soxhlet extractor. The boiling ether-insoluble fraction was a crystalline polymer and recognized as iPB. The weight percentage of ether insoluble polymer in a whole sample was reference as isotactic index (I.I.)

Differential scanning calorimetry (DSC) measurements were performed on Q2000 instrument under nitrogen atmosphere. The heating rate was 10°C min$^{-1}$ range from 40°C to 180°C. The degree of crystallinity was calculated according to the following formula:

$$X_I = \frac{\Delta H_m - \Delta H_m^0}{\Delta H_m^0}$$

Where $\Delta H_m$ was the fusion heat obtained from DSC curve, $\Delta H_m^0$ (62J/g) was the fusion heat of a perfectly crystalline iPB which crystal was [15]. Then, for the purpose of evaluating the microstructure of the iPB, self-nucleation experiments (SN)$^5,16,17$ and successive self-nucleation and annealing experiments (SSA)$^1,17,18$ were employed as follows:

Self-nucleation experiments (SN)

The self-nucleation and annealing experiment using DSC was originally reported by Fillon et al.$^{19}$ for isotactic polypropylene (PP). The successive self-nucleation and annealing (SSA) protocol employed was very similar to that reported previously. The detailed procedure was described as following: (a) Heat the sample to 180°C and maintain such temperature for 5min to erase previous thermal history. (b) Cool the sample to 30°C at 20°C/min to the initial “standard state”. (c) Heat at 20°C/min to a selected self-seeding temperature ($T_s$) located in the final melting temperature range of the sample. (d) The sample was held at this $T_s$ for 5min. This isothermal treatment at $T_s$ results in partial melting and, depending on $T_s$, in the annealing of unmelted crystals, while some of the melted species may isothermally crystallize (after being self-nucleated by the unmelted crystals). (e) Cool from $T_s$ to 30°C at a rate of 10°C/min; where the effects of SN would be revealed by the crystallization behavior of the sample. (f) Steps “c”, “d”, and “e” were repeated at progressively lower $T_s$. The number of repetitions (cycles) can be chosen to cover the entire melting range of the sample with a “standard” thermal history or a shorter range. (f) Finally, heat the sample to 180°C at 10°C/min, where the effect of the entire SN and annealing treatment would also be revealed by the melting behavior of the sample.

Successive self-nucleation/annealing experiments

(a) Heat the sample to 180°C and maintain such temperature for 5min to erase previous thermal history. (b) Cool the sample to 30°C at 20°C/min to the initial “standard state”. (c) Heat at 20°C/min to $T_s$ and maintain that temperature for 5min. The first applied $T_s$ temperature was chosen so that the polymer would only self-nucleate (i.e. $T_s$ would be high enough to melt all the crystalline regions except for small crystal fragments that can later self-seed the polymer during cooling). (d) Cool from $T_s$ to 30°C at a rate of 20°C/min. (e) Heat the sample to a new $T_s$ temperature which was 5°C lower than the previous $T_s$ and maintain that temperature for 5min. (f) Repeat steps “d” and “e” until the entire melting range of the original sample was covered. (g) Finally, the sample was heated to 180°C/min at a rate of 10°C/min.
Properties of obtained polymer were the number of alkoxy groups and size of hydrocarbon group of alkoxysilane. From Table 1, the polymerization results, the lowest catalyst activity was obtained by CPTMS and the highest catalyst activity was obtained by Donor3MP and Donor3P. As reported by Seppala et al.20, 21, the most important factor of the catalyst activity and the properties of obtained polymer were the number of alkoxy groups attached to the silicon atom, the more alkoxy groups lead to effectively deactivate the active centers of catalyst. Besides, the size of the hydrocarbon group bonded to the silicon atom was significant factor too. If the hydrocarbon group has the right size, active centers were deactivated selectively, the isotactic index increased. When R1 was methyl or isopropyl in R1R2Si(OMe)2, with the increase of the R3 size of external donors, the isotactic degree of iPB showed an increasing trend. A generally accepted mechanism was that alkoxy silane could complex with both the active sites and the cocatalysts (TEA in this work). Bulky substituents on alkoxysilane were required to prevent the external donor from leaving the catalyst surface through complexation with the cocatalyst22, therefore isotactic degree of the obtained iPB was higher. But when the steric hindrance of substituent group of external donors was too big, the complexation became weak, so the isotactic degree of iPB decreased.

The weight-average molecular weight (MW) was influenced by the structure of external donor. From Table 1, the MW increased with increasing the size of hydrocarbon groups in external donor, CPTMS exception. The MW of iPB was in range from 4.5×10^4 to 20.4×10^5 g/mol by changing the structure of external donor. The change of the molecular weight distribution was not obvious, which suggested the molecular weight distribution was correlated with Ziegler-Natta catalyst, but not directly with the external donor.

Polymer characterization

The analysis of 13C NMR spectrum

Fig. 2 13C NMR spectra of iPB using different external donors

The high-temperature 13C NMR spectrum of the iPB was shown in Figure 2. There were four peaks in the aliphatic region. The peaks observed at δ=40.3 and δ=34.8ppm had been assigned to the main chain carbons of iPB. The peak observed at δ=27.8ppm was assigned the side chain methylene carbon which directly bonded to the main chain of the isotactic iPB, the rest of peaks was belonged to the main chain of the atactic iPB. The peak observed at δ=11.0ppm was assigned to the methyl carbon in the ethylene side chain. Compared with iPB using Donor-PD, the iPB using Donor-MB had a large atactic iPB (the side chain methylene carbon which directly bonded to the main chain of the atactic iPB was appeared in 26-27ppm), which suggested the

<table>
<thead>
<tr>
<th>Samples (or Donor)</th>
<th>Activity (kg·PB·g·cat)</th>
<th>Mw (10^4 g/mol)</th>
<th>Mw (10^5 g/mol)</th>
<th>Mw/Mn</th>
<th>I.I. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor-MP</td>
<td>20.4</td>
<td>13.9</td>
<td>46.5</td>
<td>3.36</td>
<td>97.8</td>
</tr>
<tr>
<td>Donor-MB</td>
<td>13.3</td>
<td>16.7</td>
<td>48.5</td>
<td>2.90</td>
<td>96.4</td>
</tr>
<tr>
<td>Donor-MD</td>
<td>17.7</td>
<td>16.7</td>
<td>53.8</td>
<td>3.22</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-C</td>
<td>9.8</td>
<td>16.1</td>
<td>63.6</td>
<td>3.96</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-P</td>
<td>20.0</td>
<td>32.4</td>
<td>77.2</td>
<td>2.38</td>
<td>97.6</td>
</tr>
<tr>
<td>Donor-PB</td>
<td>18.0</td>
<td>25.6</td>
<td>70.2</td>
<td>2.75</td>
<td>98.0</td>
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<tr>
<td>Donor-PD</td>
<td>17.1</td>
<td>27.0</td>
<td>79.1</td>
<td>2.93</td>
<td>98.0</td>
</tr>
<tr>
<td>Donor-D</td>
<td>7.3</td>
<td>29.7</td>
<td>92.1</td>
<td>3.09</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-H</td>
<td>3.3</td>
<td>17.0</td>
<td>60.5</td>
<td>3.55</td>
<td>96.2</td>
</tr>
<tr>
<td>Donor-B</td>
<td>11.7</td>
<td>25.4</td>
<td>73.5</td>
<td>2.90</td>
<td>97.2</td>
</tr>
<tr>
<td>CPTMS</td>
<td>4.5</td>
<td>27.0</td>
<td>81.1</td>
<td>3.01</td>
<td>95.4</td>
</tr>
</tbody>
</table>

*Reaction temperature was 40°C. Gel permeation chromatography (GPC) measurements were performed using PL-GPC 220, the solvent was 1,2,4-trichlorobenzene. The isotactic index.
## Table 2 The influences of external donors on the thermal performance of iPB

<table>
<thead>
<tr>
<th>Samples (or Donor)</th>
<th>$T_m/°C$</th>
<th>$\Delta H_m/J(g)$</th>
<th>$X_c/c%$</th>
<th>$T_c/°C$</th>
<th>$\Delta H_c/J(g)$</th>
<th>$I.I./f(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor-MP</td>
<td>112.6</td>
<td>32.3</td>
<td>52.1</td>
<td>68.4</td>
<td>32.3</td>
<td>97.8</td>
</tr>
<tr>
<td>Donor-MB</td>
<td>111.2</td>
<td>29.3</td>
<td>47.3</td>
<td>62.9</td>
<td>31.8</td>
<td>96.4</td>
</tr>
<tr>
<td>Donor-MD</td>
<td>113.6</td>
<td>27.6</td>
<td>44.5</td>
<td>65.6</td>
<td>32.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-C</td>
<td>115.7</td>
<td>32.4</td>
<td>52.3</td>
<td>73.5</td>
<td>35.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-P</td>
<td>117.1</td>
<td>36.0</td>
<td>58.1</td>
<td>76.8</td>
<td>38.6</td>
<td>97.6</td>
</tr>
<tr>
<td>Donor-PB</td>
<td>116.9</td>
<td>35.2</td>
<td>56.7</td>
<td>75.6</td>
<td>37.1</td>
<td>97.0</td>
</tr>
<tr>
<td>Donor-PD</td>
<td>118.0</td>
<td>32.6</td>
<td>52.7</td>
<td>78.5</td>
<td>34.9</td>
<td>98.0</td>
</tr>
<tr>
<td>Donor-D</td>
<td>118.1</td>
<td>32.8</td>
<td>52.9</td>
<td>80.7</td>
<td>35.8</td>
<td>97.8</td>
</tr>
<tr>
<td>Donor-H</td>
<td>116.3</td>
<td>32.0</td>
<td>51.6</td>
<td>73.3</td>
<td>34.8</td>
<td>96.2</td>
</tr>
<tr>
<td>Donor-B</td>
<td>116.1</td>
<td>35.0</td>
<td>56.4</td>
<td>73.4</td>
<td>36.9</td>
<td>97.2</td>
</tr>
<tr>
<td>CPTMS</td>
<td>110.9</td>
<td>26.8</td>
<td>43.3</td>
<td>65.6</td>
<td>29.9</td>
<td>95.4</td>
</tr>
</tbody>
</table>

* Melting temperature as determined from the peak maximum value in the endothermic curve of DSC. * The value of the endothermic enthalpy as determined from DSC. * The degree of crystallization calculated from the value of the endothermic enthalpy. * The crystallization temperature as determined from the exothermic curves of DSC. * The value of the endothermic enthalpy as determined from DSC. * The isotacticity of poly(1-butene).

The stereoregularity of poly(1-butene) using the external donors with the large substituent groups were greater than the stereoregularity of poly(1-butene) using the external donor with the small substituent groups. The phenomenon was same as the results of isotactic index of iPB. According to the report of Proto and H-X. Zhang\textsuperscript{23, 24}, the stereospecificity of the catalyst system was affected by the structure of external donor and it was found that an increase of bulkiness of alkyl group had increased the isotactic. But because the stereoregularity of the obtained iPB was higher, the content of atactic iPB was very low, so the intent of peak of atactic structure was very weak, and the instrumental resolution was lower. Therefore, the stereoregularity of iPB was difficult to be accurately calculated from $^{13}$C NMR.

### The thermal and crystallization behaviors of iPB

The DSC results of poly(1-butene) are shown in Fig.3 and Table 2. As can be seen from Fig.3 and Table 2, the melting temperature and crystallization temperature of the prepared iPB showed a trend of increasing with the increase of the steric hindrance of substituent group of external donors. But when the steric hindrance of substituent group of external donors was too large, the melting point of the obtained iPB decreased to some extent with the increase of the steric hindrance of substituent group of external donors. For example, the melting temperature of iPB using Donor-H was 116.3°C which was lower than that of iPB using Donor-D and was higher than that of iPB using Donor-C. When external donor was Donor-D, the melting temperature could be reached to 118.1°C and the crystallization temperature could be reached to 80.7°C.

![Fig. 3 The DSC melting curves and crystallization curves of iPB using different external donors](image1)

![Fig. 4 The DSC crystallization and melting curve after different annealing temperature](image2)

Fillon et al.\textsuperscript{19} studied the self-nucleation behavior of iPP through the self-annealing procedures by DSC and the self-annealing temperature range divided into three domains. In Domain I or
“complete melting Domain”, the crystallization temperature \( T_c \) upon cooling from \( T_0 \) remains constant and no self-nucleation can be detected. Domain II or “self-nucleation Domain” occurs when heat treatment at \( T_s \) caused a shift in crystallization temperature to higher temperatures with decreasing crystallization temperature. Finally, in Domain III or “self-nucleation and annealing Domain”, annealing and self-nucleation took place simultaneously.

The crystallization and melting curves of SN at different annealing temperature of the Donor-P as an example were studied, as shown in Fig.4. As compared to the standard crystallization temperature obtained at the \( T_r \) temperature of 132°C, the crystallization temperature obtained at \( T_r \) temperature from 128°C to 132°C was not changed, indicating that the nucleation density of the samples remained constant in Domain I and the crystallization, nucleation, or aggregation of poly(1-butene) macromolecules did not occur.\(^{11, 25}\) When \( T_r \) was 126°C and remained constant at 126°C for 5 min, self-nucleation of poly(1-butene) occurred, its crystallization temperature was shifted to higher temperature. That’s because the unmelted component of poly(1-butene) could induced self-nucleation in the process, which could reduce the energy barrier of crystallization. Fig.4 showed that the melting peak increased obviously when the \( T_r \) temperature was 118°C, which because poly(1-butene) began self-nucleation and annealing, which suggested that the sample remain in Domain III. When the annealing temperature was lower than 119°C, the crystallization peaks became wider and the lamellae started to grow thick. The nucleation behavior of Donor-P illustrated that the minimum annealing temperature was 119°C. The optimal annealing temperature \( T_o \) of each sample was tested as above self-nucleation experiments and the results are listed in Table 3.

| Table 3 Domain- \( r \) and optimal range of \( T_o \) of each sample |
|---------------|---------------|---------------|---------------|
| Samples       | Domain-I      | Domain-II     | Domain-III    |
| Donor-MP      | \( T_r > 126 \) | \( 116 < T_r < 126 \) | \( T_r < 116 \) | 116 |
| Donor-MB      | \( T_r > 126 \) | \( 115 < T_r < 126 \) | \( T_r < 115 \) | 115 |
| Donor-MD      | \( T_r > 127 \) | \( 117 < T_r < 127 \) | \( T_r < 117 \) | 117 |
| Donor-C       | \( T_r > 127 \) | \( 119 < T_r < 127 \) | \( T_r < 119 \) | 119 |
| Donor-P       | \( T_r > 127 \) | \( 119 < T_r < 127 \) | \( T_r < 119 \) | 119 |
| Donor-PB      | \( T_r > 128 \) | \( 120 < T_r < 128 \) | \( T_r < 120 \) | 120 |
| Donor-PD      | \( T_r > 130 \) | \( 119 < T_r < 130 \) | \( T_r < 119 \) | 119 |
| Donor-D       | \( T_r > 128 \) | \( 120 < T_r < 128 \) | \( T_r < 120 \) | 120 |
| Donor-H       | \( T_r > 128 \) | \( 119 < T_r < 128 \) | \( T_r < 119 \) | 119 |
| Donor-B       | \( T_r > 128 \) | \( 119 < T_r < 128 \) | \( T_r < 119 \) | 119 |
| CPTMS         | \( T_r > 125 \) | \( 115 < T_r < 125 \) | \( T_r < 115 \) | 115 |

The study of SSA experimental parameters

Effect of annealing time on the self-nucleation behavior of poly(1-butene)

DSC thermal history was memory of the previous crystal structure of the molten polymer. It was reported that the thermal historical memory could reduce when the annealing time increased.\(^{19, 26, 27}\) Therefore, we only studied the effect of different annealing time upon SN behavior of sample Donor-P when the annealing temperature was 119°C. The results are shown in Fig.5 and Table 4. When the annealing time was \( t_0 \), the crystallization temperature \( T_c (\approx 88.9°C) \) was higher than the crystallization temperature of standard cooling. With the increasing of the annealing time, the crystallization temperature gradually decrease. But the crystallization temperature was always higher than the crystallization temperature of standard cooling. The result revealed that increasing shorter annealing time couldn’t effectively eliminate the relevant thermal historical memory when the annealing temperature was 119°C.

![Fig. 5 The crystallization behavior of SN under different annealing time of sample Donor-P](image)

| Table 4 The crystallization behavior of SN under different annealing time of sample Donor-P |
|---------------|---------------|---------------|
| \( t_0 / \text{min} \) | \( T_r / \text{°C} \) | \( \Delta H_c / \text{J/g} \) |
| Std-cooling   | 76.77         | 41.32         |
| 0             | 89.44         | 38.73         |
| 2             | 80.78         | 36.60         |
| 5             | 80.51         | 37.04         |
| 10            | 80.34         | 36.56         |
| 15            | 80.33         | 36.94         |

![Fig. 6 The SSA melting curve under different annealing time of sample Donor-P](image)
Effect of the heating and cooling rates on the SSA behavior of poly(1-butene)

![Graph showing SSA melting curve under different heating and cooling rates](Image)

For poly(1-butene), the heating and cooling rate of 20°C/min based on the annealing temperature interval was 5°C. Based on experiments, the concepts showed that the increase in heating and cooling rates (10°C/min and 20°C/min) was very similar. For low temperature melting peak, the effect of the thermal fractionation at 20°C/min was better than 10°C/min. It will appear a higher melting peak at two different heating and cooling rates, and the melting temperature (134.5°C) at 20°C/min slightly above the melting temperature (133.7°C) at 10°C/min. For poly(1-butene), the heating and cooling rate of 20°C/min could be either complete the SSA thermal fractionation or save test time.

In the SSA thermal fractionation process, the annealing temperature interval had a major impact on thermal analysis of polymers. Müller reported that an appropriate annealing interval was favorable to obtain better thermal fractionation. Fig.8 showed the SSA melting curve under of the width of the fractionation window of sample Donor-P.

![Graph showing SSA melting curve under different temperatures](Image)

The above results showed that the different parameters of SSA have the important influence on the SSA thermal fractionation process. We first determined the annealing temperature of different samples. In order to better analyze the SSA, we selected the annealing time was 10min, the annealing temperature interval was 5°C and the heating and cooling rates was 20°C/min based on the results of SN experiment.

Application of SSA to research the sequence length distribution of poly(1-butene) using different external donor

Accurate characterization of the sequence length distribution of poly(1-butene) could contribute to better understanding of the structure and properties of poly(1-butene). The crystallization behavior of poly(1-butene) was studied by the SSA thermal fractionation technology. The melting curves of iPB after SSA treatment were shown in Fig.9. Each peak of the melting point and the enthalpy of fusion ΔH_m were listed in Table 5. When R_1 was methyl in R_1R_2Si(OMe)_2, the enthalpy of fusion ΔH_m of poly(1-butene) raze from 36.7 J/g to 44.8 J/g, which increased with the increasing of volume of R_2 substituent on alkoxysilanes.

For other poly(1-butene) the phenomenon in accord with above rules, except for poly(1-butene) with Donor-H. It might be because right volume of hydrocarbon substituents on alkoxysilanes were conducive to the coordination between alkoxysilane donors and the active center, but too bulky hydrocarbon substituents on alkoxysilanes could prevent the coordination, the catalyst activity reduced, the content of ash of the poly(1-butene) increased, which lead to the high enthalpy of fusion ΔH_m.

In order to quantitatively evaluate the variations of each peak, the isotactic sequence length and distribution of poly(1-butene) were calculated by Peakfit 4.12 software. Fig.9 showed the SSA melting curve of poly(1-butene) and its fitted curves of sample by using Peakfit 4.12 software. The SSA results and the relative contents of all peaks on the SSA curve of poly(1-butene) were presented in Table 5. It has proved that the higher melting temperature on the SSA melting curves was corresponding to the higher isotacticity and isotactic sequence length in the molecular chains. As can be seen from Table 5, there were not peak 1 in...
The SSA results of poly(1-butene) samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tᵢ%</th>
<th>Tₛ/°C</th>
<th>ΔHᵢ/(J/g)</th>
<th>Tₘ₂/°C</th>
<th>n₁(%)</th>
<th>Tₘ₃/°C</th>
<th>n₂(%)</th>
<th>Tₘ₄/°C</th>
<th>n₃(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor-C</td>
<td>97.0</td>
<td>119</td>
<td>44.8</td>
<td>134.0</td>
<td>2.0</td>
<td>120.5</td>
<td>78.6</td>
<td>115.4</td>
<td>19.5</td>
</tr>
<tr>
<td>Donor-MD</td>
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<td>117</td>
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<td>133.1</td>
<td>1.3</td>
<td>120.2</td>
<td>81.1</td>
<td>114.9</td>
<td>17.6</td>
</tr>
<tr>
<td>Donor-MP</td>
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<td>132.1</td>
<td>2.1</td>
<td>119.1</td>
<td>86.2</td>
<td>113.7</td>
<td>11.7</td>
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<td>Donor-MB</td>
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<td>47.0</td>
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<td>118.1</td>
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<tr>
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<td>116</td>
<td>40.6</td>
<td>132.1</td>
<td>2.1</td>
<td>119.1</td>
<td>86.2</td>
<td>113.7</td>
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<tr>
<td>Donor-D</td>
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<td>47.0</td>
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<td>121.9</td>
<td>81.0</td>
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<tr>
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<td>44.5</td>
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<td>120.2</td>
<td>81.1</td>
<td>114.9</td>
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<tr>
<td>CPTMS</td>
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The SSA results of poly(1-butene) samples after SSA thermal fractionation

<table>
<thead>
<tr>
<th>Samples</th>
<th>L₁/nm</th>
<th>L₂/nm</th>
<th>L₃/nm</th>
</tr>
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<tr>
<td>Donor-C</td>
<td>24.68</td>
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<td>2.50</td>
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<tr>
<td>Donor-MD</td>
<td>17.28</td>
<td>3.26</td>
<td>2.45</td>
</tr>
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<td>Donor-MP</td>
<td>12.96</td>
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<td>2.31</td>
</tr>
<tr>
<td>Donor-MB</td>
<td>2.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Donor-PD</td>
<td>22.54</td>
<td>3.65</td>
<td>2.85</td>
</tr>
<tr>
<td>Donor-P</td>
<td>25.92</td>
<td>3.68</td>
<td>2.76</td>
</tr>
<tr>
<td>Donor-PB</td>
<td>28.80</td>
<td>3.78</td>
<td>2.88</td>
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<tr>
<td>Donor-MP</td>
<td>12.96</td>
<td>3.05</td>
<td>2.31</td>
</tr>
<tr>
<td>Donor-D</td>
<td>24.68</td>
<td>3.70</td>
<td>2.80</td>
</tr>
<tr>
<td>Donor-PD</td>
<td>22.54</td>
<td>3.65</td>
<td>2.85</td>
</tr>
<tr>
<td>Donor-MD</td>
<td>17.28</td>
<td>3.26</td>
<td>2.45</td>
</tr>
<tr>
<td>CPTMS</td>
<td>2.88</td>
<td></td>
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</tr>
</tbody>
</table>

The lamellar thickness can be estimated from the SSA results with Thomson-Gibbs equation

\[ T_m = T_m^o \left( 1 - \frac{2a}{\Delta H_a L} \right) \]

Where \( T_m^o = 409.25 \)K (equilibrium melting temperature), \( \Delta H_a = 1.35 \times 10^3 \)J/m³, \( \sigma = 17.1 \times 10^{-2} \)J/m² (surface energy) and \( L \) is the lamellar thickness. The lamellae thickness of IPB after SSA thermal fractionation was calculated and listed in Table 6. When
R₁ was methyl in R₁R₂Si(OMe)₂, with the increasing of the steric hindrance of R₂, the lamellae thickness of iPB gradually increased. But when R₁ was isopropyl, the lamellae thickness of iPB using Donor-P, Donor-PD and Donor-PB, which was higher than the lamellae thickness of iPB using Donor-MP. The lamellae thickness of iPB prepared using Donor-PB was the thickest (the lamellar thickness of peak 1 was 28.80nm, the lamellar thickness of peak 2 was 3.78nm, the lamellar thickness of peak 3 was 2.88nm). When R₁ and R₂ were same substituent, the lamellae thickness of peak 2 and peak 3 was same, but the lamellae thickness of peak 1 was different, and the thickest lamellae thickness of peak 1 of iPB using Donor-P was 25.92.

Moreover, in order to further the analysis, we introduce the terms of “arithmetic average Lₐ”, the “weighted average Lₐ”, and the broadness index Lₐ/Lₙ.

$$Lₐ = \frac{n₁L₁ + n₂L₂ + \cdots n_jL_j}{n₁ + n₂ + \cdots n_j} = \sum f_iL_i$$

$$Lₜ = \frac{n₁L₁^2 + n₂L₂^2 + \cdots n_jL_j^2}{n₁L₁ + n₂L₂ + \cdots n_jL_j} = \sum f_iL_i^2$$

where nᵢ was the normalized peak area, and the Lₐ was the lamellae thickness for each fraction. The results of all samples are listed in Table 7. As can be seen from Table 7, when R₁ was methyl in R₁R₂Si(OMe)₂, with the increasing of the steric hindrance of R₂, the Lₐ, nₐ, and I increases gradually. But when R₁ was isopropyl, the varied tendency of the Lₐ, nₐ, and I doesn’t show the regularity. It is found that iPB prepared using Donor-PB has the highest isotactic component and the lower medium component relative to other iPB, but the amount of the medium component was higher, therefore, the sequence length distribution was broader.

### Table 7 Lamellar thickness statistical parameters of iPB samples prepared by the different external donors

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lₐ/nm</th>
<th>Lₜ/nm</th>
<th>I = Lₜ/Lₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor-C</td>
<td>6.15</td>
<td>3.59</td>
<td>1.71</td>
</tr>
<tr>
<td>Donor-MD</td>
<td>4.11</td>
<td>3.30</td>
<td>1.25</td>
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<tr>
<td>Donor-MP</td>
<td>3.84</td>
<td>3.17</td>
<td>1.21</td>
</tr>
<tr>
<td>Donor-MB</td>
<td>2.94</td>
<td>2.92</td>
<td>1.01</td>
</tr>
<tr>
<td>Donor-PD</td>
<td>7.03</td>
<td>4.17</td>
<td>1.69</td>
</tr>
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<td>Donor-P</td>
<td>7.00</td>
<td>3.93</td>
<td>1.78</td>
</tr>
<tr>
<td>Donor-PB</td>
<td>8.35</td>
<td>4.31</td>
<td>1.94</td>
</tr>
<tr>
<td>Donor-MP</td>
<td>3.84</td>
<td>3.17</td>
<td>1.21</td>
</tr>
<tr>
<td>Donor-D</td>
<td>7.00</td>
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<td>1.69</td>
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<td>Donor-MD</td>
<td>4.11</td>
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<td>1.25</td>
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<tr>
<td>CPTMS</td>
<td>2.80</td>
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<td>1.01</td>
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<tr>
<td>Donor-P</td>
<td>7.00</td>
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<td>1.78</td>
</tr>
<tr>
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<td>4.09</td>
<td>1.64</td>
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<tr>
<td>Donor-H</td>
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</tr>
<tr>
<td>Donor-B</td>
<td>5.98</td>
<td>3.93</td>
<td>1.52</td>
</tr>
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</table>

### Conclusions

In this paper, poly(1-butene) was prepared by Ziegler-Natta catalysts using silane external donor. The influence of steric hindrance of external donor on the structure of poly(1-butene) was studied by DSC and ¹³C NMR. The crystallization behavior and sequence length distribution of poly(1-butene) samples were studied by the successive self-nucleation and annealing calorimetric technique. It was found that the proper annealing time tₛ, annealing temperature interval and heating and cooling rates could enhance the separation of the different crystalline components. The results showed that iPB has higher isotacticty and stereoregularity by the bulk polymerization. The SSA results showed the melting temperature of iPB increased with the increasing of the steric hindrance of external donor, the subtle differences in the temperature has a big impact on the lamellae thickness of iPB. When R₁ was methyl in R₁R₂Si(OMe)₂, the Lₐ, nₐ, and I increased gradually with increasing of the steric hindrance of R₂. But, when R₁ was isopropyl, the tendency of the Lₐ, nₐ, and I had no regularity.

### Acknowledgements
The authors gratefully acknowledge the financial supports provided by the National Natural Science Foundation of China (No. 51073170, 50703044, 51403216).

Notes and references

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GRAPHICAL ABSTRACT

Application of successive self-nucleation and annealing (SSA) to poly(1-butene) prepared by Ziegler-Natta catalysts with different external donors

Tao Zheng, Qian Zhou, Qian Li, Huayi Li, Liaoyun Zhang, Youliang Hu

The SSA thermal fractionation technology could analyze the accurate characterization of the sequence length distribution of iPB.