A new post-metallocene catalyst for alkene polymerization: copolymerization of ethylene and 1-hexene with titanium complexes bearing \(N,N\)-dialkylcarbamato ligands

Mohammad Hayatifar, a Guido Pampaloni, a Luca Bernazzani, a Carmine Capacchione, b Yury V. Kissin c and Anna Maria Raspolli Galletti a,∗

Abstract

A new type of post-metallocene polymerization catalyst based on titanium complexes with \(N,N\)-dialkylcarbamato ligands was used to copolymerize ethylene and 1-hexene. These easy-to-synthesize and stable complexes in combination with different organoaluminium co-catalysts produce random ethylene/1-hexene copolymers characterized by a broad molecular weight distribution and high 1-hexene incorporation, as confirmed by SEC, DSC and \(^{13}\)C NMR analysis. The influence of the main reaction parameters on the polymerization reactions was studied including the type of catalyst components, solvent, temperature, the ethylene partial pressure and the [Al]/[Ti] ratio in the catalyst. A higher activity and a higher 1-hexene incorporation were achieved with AlMe3-depleted methylalumoxane as co-catalyst and chlorobenzene as solvent.

Keywords: ethylene/1-hexene copolymerization; \(N,N\)-dialkylcarbamato ligands; organoaluminium co-catalyst; titanium complex

INTRODUCTION

Ethylene/1-alkene copolymers are commercially important materials with a wide range of applications.1−5 These copolymers are most commonly produced with titanium- or vanadium-based Ziegler–Natta catalysts or with single-site metallocene catalysts.3−5 At the present time, the focus of attention in alkene polymerization chemistry has shifted to soluble post-metallocene catalysts based on a variety of multi-dentate complexes of transition metals. Several studies describing the use of different non-metallocene complexes of group 4 transition metals in ethylene copolymerization reactions have been reported in the literature;6−19 some of the catalysts are employed on an industrial scale.8,10

Complexes bearing \(N,N\)-dialkylcarbamato ligands have been known since 1970.20 However, relatively little has been reported on the use of these complexes as catalyst precursors in alkene polymerization reactions although the complexes can potentially provide new opportunities for the synthesis of alkene polymers because of their high yield synthesis and easy handling.

As a part of our investigation of the coordination behavior of titanium \(N,N\)-dialkylcarbamato complexes, we have found that these compounds, upon activation with methylalumoxane (MAO), catalyze ethylene homopolymerization reactions.21 As an expansion of this preliminary work, we synthesized two \(\text{Ti(O}_2\text{CNR}_2)_4\) complexes with \(R = \text{Et} \) (I) and \(R = \text{Me} \) (II) and the mixed chlorocarbamato derivative \(\text{Ti(O}_2\text{CNMe})_2\text{Cl}_2 \) (III) and explored their catalytic potential in copolymerization reactions of ethylene with 1-hexene (Scheme 1). The effects of the principal reaction conditions such as the type of co-catalyst and solvent, the polymerization temperature, the [Al]/[Ti] molar ratio and the monomer pressure on the polymerization behavior were investigated.

EXPERIMENTAL

Materials

All manipulations of air- and water-sensitive compounds were performed under dry nitrogen using standard Schlenk and vacuum-line techniques. Ethylene (>99%; Rivoira, Torino, Italy) was used as received. Toluene (Baker, Deventer, Holland) and chlorobenzene (Fluka, Steinheim, Germany) were dried by refluxing for 8 h over a K/Na alloy and CaH2, respectively, and distilled under dry nitrogen before use. TiCl4 (Fluka), MAO (toluene solution, 10 wt%), ethylaluminium sesquichloride (Et3Al2Cl3, 97%) and Al(i-Bu)3 (toluene solution, 25 wt%) were purchased from...
Copolymerization reactions of ethylene and 1-hexene

Precursors I, II and III are very soluble in the polymerization medium and no solid formation was ascertained even after several hours of aging of the Ti precursor/DMAO/PhCl mixture.

Ethylene/1-hexene (E/H) copolymerization reactions were conducted in a three-necked 250-mL round-bottom flask under magnetic stirring when at a low ethylene partial pressure ($P_2$). A solvent was introduced into the flask and was saturated with ethylene at 0.1 MPa at the required temperature; then required amounts of 1-hexene, a co-catalyst and precursor solution were added to keep the total volume of the reaction mixture equal to 65 mL.

The polymerization reactions were terminated by adding acidified methanol; the polymers were separated by pouring the reaction mixtures into large excess of methanol. Precipitated polymers were filtered, washed and dried under vacuum.

E/H copolymerization reactions at a high $P_2$ were carried out in a 250-mL stainless steel reactor. All the components were transferred to the reactor under an ethylene atmosphere. After addition of required amounts of 1-hexene, a co-catalyst and a Ti complex, the reactor was heated and pressurized with ethylene.

Analytical procedures

Molecular weights of E/H copolymers and their molecular weight distributions were determined by SEC. The measurements were carried out with a high temperature Waters GPC V2000 system equipped with a differential refractometer as a detector. The experimental conditions were as follows: three PL Gel Olexis columns, o-dichlorobenzene as a mobile phase, a flow rate of 0.8 mL min$^{-1}$ and a column temperature of 145 °C. SEC calibration was carried out using 18 polystyrene standards with a narrow molecular weight distribution and with molar weights ranging from 162 to 5.6 × 10$^6$ g mol$^{-1}$. Resolution of SEC curves into elemental (Flory) components was carried out with the Scientist program (MicroMath Scientific Software), as described elsewhere.$^{26}$ Figures 1, 3 and 4 later show three examples of the resolution.

IR spectra of thin films of the E/H copolymers (obtained by die-casting at 160 °C) were recorded in the 1400–1265 cm$^{-1}$ range with a Spectrum GX Perkin-Elmer spectrophotometer combined with an Autoimage Perkin-Elmer microscope. Copolymer compositions were calculated from the absorbance ratio of the CH$_3$ bending mode (1380 cm$^{-1}$) and the CH$_2$ wagging mode (1370 cm$^{-1}$) using a calibration curve based on E/H copolymer standards of known compositions (determined by $^{13}$C NMR) kindly supplied by Polimeri Europa S.p.A.

Copolymer samples for NMR experiments were prepared directly in NMR tubes by adding o-dichlorobenzene (Aldrich, ≥99%) to weighed amounts of dry polymers to produce ca 5% solutions. The samples were heated at >80 °C in a water bath for 1 h to achieve complete dissolution of the copolymers. The $^{13}$C NMR experiments were carried out with a Bruker AMX-300 WB spectrometer at 75.13 MHz using a 10 mm probe head. The spectra were recorded at 90 °C at a 20° pulse of 2 μs and a delay time of 6 s; 5000 scans were collected to obtain quantitative spectra. Chemical shifts were referenced to an external SiMe$_4$ standard. Relative signal intensities in each spectrum were obtained by spectral deconvolution using the SPORT-NMR software.$^{27}$ The spectral assignment and the determination of the monomer sequence distribution were carried out according to Hsieh and Randall.$^{28}$

DSC melting curves of the copolymers were recorded with a Perkin-Elmer Pyris Diamond DSC instrument. First, the samples were melted at 140 °C and then slowly crystallized and annealed by cooling to ca 30 °C at a rate of 0.5 °C min$^{-1}$. The melting curves were then recorded at a heating rate of 2 °C min$^{-1}$.

RESULTS AND DISCUSSION

Copolymerization reactions with complexes I–III activated with Et$_3$Al$_2$Cl$_3$ and Al'Bu$_3$

Complexes I, II and III were tested as catalyst precursors in E/H copolymerization reactions using mixtures of Et$_3$Al$_2$Cl$_3$ and Al'Bu$_3$ as co-catalysts. The results are reported in Table 1. The data show that all the precursors exhibit moderate catalytic activity and that these catalyst systems copolymerize 1-hexene with ethylene quite well.

Any comparison of catalyst activity in ethylene/1-alkene copolymerization reactions based on the product yield is complicated by the fact that different copolymers contain different amounts of 1-alkenes. To make such comparisons more realistic,
The activity of complex III in the E/H copolymerization reactions strongly depends on the polymerization temperature. A decrease in activity was observed when the polymerization temperature was increased from 30 to 50 °C (run 4 versus run 1); the productivity was reduced from 11.8 to 7.7 kg mol\textsuperscript{-1} h\textsuperscript{-1}, thus indicating that the Ti-based active species in this catalyst system are thermolabile.

The solvent plays a key role in these polymerization reactions. When toluene was employed as a solvent instead of chlorobenzene (run 5 versus run 1), the catalyst productivity decreased from 11.8 to 3.7 kg mol\textsuperscript{-1} h\textsuperscript{-1} and the ability of the catalyst to incorporate 1-alkenes also decreased; the $C_{\text{Hex}}^{\text{cop}}$ value decreased from 28 to 20.6 mol\%. This effect of the solvent’s dielectric constant on the copolymerization ability seems to be universal\textsuperscript{30}

When complex II was used as a precursor (run 7) instead of complex III (run 1) under the same reaction conditions, a small increase in productivity was observed, 16.3 versus 11.8 kg mol\textsuperscript{-1} h\textsuperscript{-1}. Complex I (run 8 in Table 1) showed an even higher catalytic activity, 20.9 kg mol\textsuperscript{-1} h\textsuperscript{-1}, and a higher level of 1-hexene incorporation, ca 28 mol\%.

Earlier, some of us reported results of E/H copolymerization reactions with a titanium carboxylate complex L\textsuperscript{IV}TiCl\textsubscript{2} similar in structure to complex III in this study\textsuperscript{31}. Two E/H copolymerization experiments in toluene, run 5 in Table 1 and run 31 in ref. 31, were carried out with the two complexes under the same experimental conditions. A comparison of the results shows that both the L\textsuperscript{IV}TiCl\textsubscript{2} complexes have similar ethylene consumption rates (2.1 and 1.6 kgE mol\textsuperscript{-1} h\textsuperscript{-1}) but the Al/N-dialkylcarbamato complex III incorporates 1-hexene four times better than the carboxylate complex; $C_{\text{Hex}}^{\text{cop}}$ values are 20 and 5 mol\%, respectively.

### Table 1. Ethylene-1-hexene copolymerization with carbamato Ti complexes activated with Et\textsubscript{3}Al\textsubscript{2}Cl\textsubscript{3} and Al(\textsuperscript{Bu\textsubscript{3}}\textsuperscript{a})

<table>
<thead>
<tr>
<th>Run</th>
<th>Complex (\textmu mol)</th>
<th>$P_E$ (MPa)</th>
<th>$C_{\text{Hex}}$ (mol L\textsuperscript{-1})</th>
<th>Activity$^b$</th>
<th>$C_{\text{Hex}}^{\text{cop}}$ (mol%)</th>
<th>Conv$_{\text{Hex}}$ (%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J g\textsuperscript{-1})</th>
<th>$M_w \times 10^{-3}$ (Da)</th>
<th>$M_w/M_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>III (20)</td>
<td>0.1</td>
<td>3.70</td>
<td>11.8 (5.4)</td>
<td>28.2</td>
<td>28</td>
<td>3.2</td>
<td>119.1</td>
<td>6.8</td>
<td>371</td>
</tr>
<tr>
<td>2</td>
<td>III (20)</td>
<td>0.1</td>
<td>0.62</td>
<td>7.5 (6.3)</td>
<td>6.8</td>
<td>6</td>
<td>3.6</td>
<td>121.2</td>
<td>63.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>III (25)</td>
<td>1.0</td>
<td>3.70</td>
<td>24.5 (23.1)</td>
<td>2.0</td>
<td>2</td>
<td>0.9</td>
<td>126.1</td>
<td>117.5</td>
<td>1086</td>
</tr>
<tr>
<td>4$^c$</td>
<td>III (14)</td>
<td>0.1</td>
<td>3.70</td>
<td>7.7 (3.8)</td>
<td>24.5</td>
<td>25</td>
<td>1.4</td>
<td>119.9</td>
<td>15.3</td>
<td>913</td>
</tr>
<tr>
<td>5$^d$</td>
<td>III (14)</td>
<td>0.1</td>
<td>3.70</td>
<td>3.7 (2.1)</td>
<td>20.6</td>
<td>21</td>
<td>0.6</td>
<td>120.7</td>
<td>25.1</td>
<td></td>
</tr>
<tr>
<td>6$^e$</td>
<td>III (17)</td>
<td>0.1</td>
<td>0.62</td>
<td>11.1 (9.0)</td>
<td>7.0</td>
<td></td>
<td>2.7</td>
<td>121.0</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>II (20)</td>
<td>0.1</td>
<td>3.70</td>
<td>16.3 (8.4)</td>
<td>23.8</td>
<td></td>
<td>3.9</td>
<td>120.3</td>
<td>26.0</td>
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</tr>
<tr>
<td>8</td>
<td>I (20)</td>
<td>0.1</td>
<td>3.70</td>
<td>20.9 (9.9)</td>
<td>27.8</td>
<td>26</td>
<td>5.3</td>
<td>118.9</td>
<td>10.2</td>
<td>350</td>
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<tr>
<td>9</td>
<td>TiCl\textsubscript{4} (20)</td>
<td>0.1</td>
<td>3.70</td>
<td>10.4 (5.5)</td>
<td>22.8</td>
<td>22</td>
<td>2.4</td>
<td>121.1</td>
<td>31.7</td>
<td></td>
</tr>
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</table>

$^a$ Reaction conditions: [Et\textsubscript{3}Al\textsubscript{2}Cl\textsubscript{3}]/[Ti] = 3 mol mol\textsuperscript{-1}; [Al(\textsuperscript{Bu\textsubscript{3}})]/[Ti] = 50 mol mol\textsuperscript{-1}; reaction time 5 h; temperature 30 °C; solvent chlorobenzene; total volume 65 mL.

$^b$ The first number is the combined activity, kg mol\textsuperscript{-1} h\textsuperscript{-1}; in parenthesis is the ethylene consumption, kgE mol\textsuperscript{-1} h\textsuperscript{-1}, calculated using Eqn (1).

$^c$ Temperature 50 °C.

$^d$ Solvent toluene.

$^e$ Reaction time 2.5 h.

Catalyst productivity values were recalculated to estimate only consumption of ethylene in the copolymerization reactions:

$$\text{ethylene consumption (kgE mol}^{-1}\text{h}^{-1}) = \text{activity} \times \left[1 - 0.01C_{\text{Hex}}^{\text{cop}}\right] / \left[1 + 0.01C_{\text{Hex}}^{\text{cop}} (\text{MW}_{\text{Hex}}/\text{MW}_{E} - 1)\right]$$

where $C_{\text{Hex}}^{\text{cop}}$ is the mole percent of 1-hexene in the copolymer and MW$_{\text{Hex}}$ and MW$_E$ are the molecular weights of 1-hexene and ethylene, respectively. Data on ethylene consumption are provided in parentheses in Table 1.

A decrease of the amount of 1-hexene in the feed (run 2 versus run 1) resulted in a reduced total productivity, 7.5 kg mol\textsuperscript{-1} h\textsuperscript{-1}, and in an expected decrease of the 1-hexene content in the product. However, this reduction in productivity is only apparent; the calculated ethylene consumption in runs 1 and 2 is similar, ca 5.4 and 6.3 kgE mol\textsuperscript{-1} h\textsuperscript{-1}.

As expected, increasing the $P_E$ value to 1 MPa (run 3 versus run 1) led to an increase in productivity and a decrease in the 1-hexene content in the copolymer. Overall, these effects are similar to those observed in metallocene catalysis\textsuperscript{4,29}. However, the increase in the amount of consumed ethylene was lower than expected for a 10-fold increase in the ethylene concentration in solution, ca 23 versus ca 5 kgE mol\textsuperscript{-1} h\textsuperscript{-1}, suggesting that increasing the ethylene concentration suppresses the activity of some active centers.

An increase of the reaction time from 2.5 to 5 h (run 2 versus run 6) led to a small decrease in the averaged ethylene consumption rate (ca 9 versus ca 6 kgE mol\textsuperscript{-1} h\textsuperscript{-1}) without any significant change in the 1-hexene incorporation degree. This result suggests that the number of active centers at 30 °C gradually decreases over time.
An increase of the 1-hexene concentration in the reaction mixture leads to a gradual increase of the combined catalyst activity and the ethylene consumption (runs 10–12).\(^\text{32}\)

An increase in \(P_E\) (run 15 versus run 10) leads both to a large increase in productivity and ethylene consumption and to an expected decrease in the 1-hexene content in the copolymer.

The activity of the III—MAO system depends on the [MAO]/[Ti] molar ratio (runs 13, 10 and 14). Similarly to metallocene-based catalysts,\(^\text{33}\) an increase of the [MAO]/[Ti] molar ratio from 150 to 300 results in a large gain in productivity, from 48 to 86 kg mol\(^{-1}\) h\(^{-1}\), whereas a further increase of the [MAO]/[Ti] ratio to 600 does not affect the catalyst productivity any more.

Similarly to the data in Table 1, the catalytic activity decreases with reaction temperature.

The nature of the solvent is an important factor in these reactions as well. When the copolymerization reactions were carried out under the same reaction conditions (runs 10, 18 and 19), the switch from chlorobenzene to toluene and to a lower valence state, which is less active in the polymerization reaction and much less efficient in 1-hexene incorporation.\(^\text{36}\)

Copolymerization reactions with complexes \textbf{I} and \textbf{II} (runs 21–23) resulted in catalysts of significantly lower productivity, and a conventional Ziegler catalyst based on TiCl\(_4\) (run 24) showed an even lower activity.

### Copolymer structure

Several of the prepared copolymers were analyzed by SEC, DSC and \(^{13}\)C NMR. The analytical results showed that the performance of the catalysts based on Ti complexes with \(N,N\)-dialkylcarbamato ligands can be most readily interpreted when these catalysts are used in E/H copolymerization reactions at a relatively high \(P_E\). Figure 1 shows the SEC curve of the copolymer prepared in run 3 with the III–Et\(_3\)Al\(_2\)Cl\(_3\)/AlBu\(_3\) catalyst at a high \(P_E\) and, respectively, at a relatively low \(C_{\text{Hex}}/C_E\) monomer ratio of ca 4. A comparison of the experimental curve and the calculated curve for a single Flory component (a Flory component is defined as a copolymer material) was produced. These changes suggest that AlMe\(_3\) present in commercial MAO may reduce Ti in the complexes to a lower valence state, which is less active in the polymerization reaction and much less efficient in 1-hexene incorporation.\(^\text{36}\)

When MAO was replaced with DMAO (run 20 versus run 10), a much higher productivity was observed and a copolymer containing over 30 mol% of 1-hexene (a rubbery amorphous material) was produced. These changes suggest that AlMe\(_3\) present in commercial MAO may reduce Ti in the complexes to a lower valence state, which is less active in the polymerization reaction and much less efficient in 1-hexene incorporation.\(^\text{36}\)

<table>
<thead>
<tr>
<th>Run</th>
<th>Complex (µmol)</th>
<th>(P_E) (MPa)</th>
<th>(C_{\text{Hex}}) (mol L(^{-1}))</th>
<th>Activity(^a)</th>
<th>IR</th>
<th>NMR</th>
<th>Conv(_{\text{Hex}}) (%)</th>
<th>(T_m) (°C)</th>
<th>(\Delta H_m) (J g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>III (20)</td>
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<td>2.46</td>
<td>86 (53)</td>
<td>17.8</td>
<td>17</td>
<td>2.5</td>
<td>85.0(^b)</td>
<td>25.5</td>
</tr>
<tr>
<td>11</td>
<td>III (20)</td>
<td>0.1</td>
<td>1.23</td>
<td>69 (44)</td>
<td>16.9</td>
<td>16</td>
<td>3.7</td>
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</tr>
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<td>0.62</td>
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<td>-</td>
<td>5.1</td>
<td>111.9</td>
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<td>13</td>
<td>III (20)(^d)</td>
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<td>2.46</td>
<td>48 (27)</td>
<td>21.5</td>
<td>-</td>
<td>1.6</td>
<td>83.2</td>
<td>20.7</td>
</tr>
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<td>14</td>
<td>III (20)(^k)</td>
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<td>2.46</td>
<td>74 (46)</td>
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<td>-</td>
<td>2.4</td>
<td>88.0</td>
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<td>2.46</td>
<td>423 (308)</td>
<td>10.9</td>
<td>11</td>
<td>8.5</td>
<td>116.5(^5)</td>
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<td>373 (258)</td>
<td>12.9</td>
<td>-</td>
<td>8.5</td>
<td>115.6</td>
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<td>2.46</td>
<td>1093 (842)</td>
<td>8.7</td>
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<td>11.1</td>
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<td>117.0</td>
<td>71.1</td>
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<td>19</td>
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<td>2.46</td>
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<td>&gt; 30</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>2.46</td>
<td>309 (130)</td>
<td>&gt; 30</td>
<td>-</td>
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<td>21</td>
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<td>2.46</td>
<td>8</td>
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<td>1.0</td>
<td>2.46</td>
<td>44 (35)</td>
<td>7.9</td>
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<td>23</td>
<td>I (20)</td>
<td>0.1</td>
<td>2.46</td>
<td>70 (39)</td>
<td>21.4</td>
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<td>2.3</td>
<td>83.7</td>
<td>22.0</td>
</tr>
<tr>
<td>24</td>
<td>TiCl(_4) (20)</td>
<td>0.1</td>
<td>2.46</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: [AI]/[Ti] = 300; temperature 25 °C; reaction time 0.5 h; solvent chlorobenzene; total volume 65 mL.

\(^b\) The first number is the combined activity, kg molTi\(^{-1}\) h\(^{-1}\); in parenthesis is the ethylene consumption, kgE molTi\(^{-1}\) h\(^{-1}\), calculated using Eqn (1).

\(^c\) Temperature 50 °C.

\(^d\) Reaction time 10 min.

\(^e\) Solvent toluene.

\(^f\) Solvent n-heptane.

\(^g\) Co-catalyst DMAO.

\(^h\) \(M_n = 186 000, M_w/M_n = 3.9\).

\(^i\) \(M_n = 706 000, M_w/M_n = 2.6\).

\(^j\) \([AI]/[Ti] = 150\).

\(^k\) \([AI]/[Ti] = 600\).
Under high $P_E$ the catalyst produces a copolymer material (component V in Table 3) with a very high $M_w$ of ca 1.2 × 10^6. Judging by the relationship between the ($C_{\text{Hex}}/C_E$)_{monomer} ratio in this experiment and the copolymer composition (using a simplified copolymerization equation) \(33\)

\[
(C_{\text{Hex}}/C_E)_{\text{copol}} = (1/r_1) (C_{\text{Hex}}/C_E)_{\text{monomer}}
\]

the reactivity ratio $r_1$ for the E/H pair for this type of active center is ca 200, which implies a relatively poor ability of this center to copolymerize 1-hexene with ethylene. As a comparison, the $r_1$ values for the E/H pair in the case of metallocene catalysts vary from 20–30 to 50–60 according to different estimations. \(33\)

Figure 2 shows the SEC melting curve of the same copolymer (produced in run 3) and its resolution into melting curves of individual components. The SEC resolution was carried out according to the technique described in ref. 37. Superficially, this melting curve has a single, relatively narrow melting peak with a maximum at 126.9 °C, which is typical for melting of ethylene copolymers produced with single-center catalysts and containing low fractions of a 1-alkene. \(37\) However, the resolution of the SEC data in Fig. 2 shows that this product is a mixture of several components with similar compositions, their ($C_{\text{Hex}}/C_E$)_{copol} values ranging from ca 1.4 mol% for the component with the highest $T_m$ to ca 2.2 mol%. The average ($C_{\text{Hex}}/C_E$)_{copol} value for the mixture calculated according to ref. 37 (1.8 mol%) is the same as the experimentally measured average ($C_{\text{Hex}}/C_E$)_{copol} value.

This nearly single-center nature of the III–Et₃Al₂Cl₃/Al′Bu₃ catalyst is an exception; it was found only in copolymerization reactions at a high $P_E$. When $P_E$ in the copolymerization reaction with this catalytic system was decreased 10 times (run 1 in Table 1), the ethylene consumption rate decreased merely by a factor of ca 4. The difference can be explained if one assumes that the catalyst contains several types of active centers but that the activity of some of them is suppressed in the presence of ethylene. The SEC analysis supports this assumption. Figure 3 gives the SEC curve of the E/H copolymer produced in run 1 and its resolution into individual Flory components. Obviously, when the same catalyst is used at a low $P_E$ and, respectively, at a relatively high ($C_{\text{Hex}}/C_E$)_{monomer} ratio, several types of active centers are generated.

Table 3 gives the results of the SEC curve resolution into individual Flory components for several E/H copolymers. Three of them were prepared with the catalyst system containing complex III and the Et₃Al₂Cl₃/Al′Bu₃ co-catalyst. The data for run 1 (see also

![Figure 2](image-url) DSC curve of the copolymer produced in run 3 and its resolution into elemental components.\(37\)

![Figure 3](image-url) SEC curve of the copolymer produced in run 1 (points) and its resolution into Flory components.
Table 3. Flory components in E/H copolymers

<table>
<thead>
<tr>
<th>Run</th>
<th>Complex</th>
<th>Co-catalyst</th>
<th>Conditions</th>
<th>$C_{Hex/\text{Copol}}$</th>
<th>Flory Component</th>
<th>$M_w$</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>III</td>
<td>$\text{Et}_3\text{Al}_2\text{Cl}_3/\text{AlBu}_3$</td>
<td>30 °C, 5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 39$; 28.0 mol%</td>
<td>I</td>
<td>14 600</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>II</td>
<td>55 000</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III</td>
<td>163 800</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
<td>458 500</td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V</td>
<td>1 308 000</td>
<td>13.4</td>
</tr>
<tr>
<td>3</td>
<td>III</td>
<td>$\text{Et}_3\text{Al}_2\text{Cl}_3/\text{AlBu}_3$</td>
<td>30 °C, 5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 4$; 2.0 mol%</td>
<td>V</td>
<td>1 168 000</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>III</td>
<td>$\text{Et}_3\text{Al}_2\text{Cl}_3/\text{AlBu}_3$</td>
<td>50 °C, 5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 49$; 24.5 mol%</td>
<td>II</td>
<td>43 050</td>
<td>8.4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III</td>
<td>243 500</td>
<td>12.6</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>V</td>
<td>1 065 000</td>
<td>79.0</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>$\text{Et}_3\text{Al}_2\text{Cl}_3/\text{AlBu}_3$</td>
<td>30 °C, 5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 39$; 26.0 mol%</td>
<td>Ia</td>
<td>1 720</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Iia</td>
<td>6 640</td>
<td>9.2</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>I</td>
<td>20 400</td>
<td>17.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>II</td>
<td>54 100</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III</td>
<td>151 800</td>
<td>20.2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
<td>428 700</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V</td>
<td>1 198 500</td>
<td>10.4</td>
</tr>
<tr>
<td>10</td>
<td>III</td>
<td>MAO</td>
<td>25 °C, 0.5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 26$; 17.0 mol%</td>
<td>I</td>
<td>22 500</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>II</td>
<td>76 300</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III</td>
<td>193 300</td>
<td>43.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
<td>589 500</td>
<td>14.1</td>
</tr>
<tr>
<td>15</td>
<td>III</td>
<td>MAO</td>
<td>25 °C, 0.5 h, $(C_{Hex/\text{Copol}})_{\text{mon}} \approx 2.5$; 11.0 mol%</td>
<td>II</td>
<td>55 100</td>
<td>2.7</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
<td>227 600</td>
<td>19.1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V</td>
<td>887 500</td>
<td>78.2</td>
</tr>
</tbody>
</table>

* Ethylene concentration is estimated based on ethylene solubility in benzene and toluene.

$M_w \approx 1.0 \times 10^6$, is very similar to that of the Flory component V in the product formed in runs 3 and 1 at 30 °C. In general, the values of the reactivity ratios change relatively weakly with temperature. If the $r_1$ values for the centers producing Flory components II and III in run 4 are assumed to be the same as in run 1 at 30 °C, ca 120, and the $r_3$ value for the center producing Flory component V is assumed to be the same as in run 3, ca 200, the average $C_{Hex/\text{Copol}}$ value for the material formed in run 4 should be ca 22 mol%, quite close to the experiment.

The E/H copolymer in run 8 was produced under the same conditions as in run 1 but using a different Ti carbamato complex, I, also activated with the $\text{Et}_3\text{Al}_2\text{Cl}_3/\text{AlBu}_3$ co-catalyst. A comparison of the SEC resolution data for the products formed in runs 8 and 1 (Table 3) shows that both catalyst systems contain approximately the same set of active centers in terms of their $k_tM/k_p$ and $r_1$ values but in slightly different proportions. In addition, the use of complex I results in the formation of two more types of active centers generating small amounts of Flory components with low $M_w$, Ia and Ib.

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**Figure 4.** SEC curve of the copolymer produced at 50 °C in run 4 (points) and its resolution into Flory components.

**Figure 5.** $^{13}$C NMR spectrum of the E/H copolymer produced in run 8 ($C_{Hex/\text{Copol}} = 26$ mol%).
Overall, the structural analysis of E/H copolymers produced with complexes I–III activated with Et3Al2Cl3/Al′Bu3 mixtures showed that all these catalysts under most experimental conditions have the multi-center nature. It is difficult to specify the real active species in such catalytic systems. We propose that the generation of several types of active centers, which manifests itself in a broad molecular weight distribution of the copolymers, can be attributed to a highly versatile and fluxional character of the precatalysts. In fact, N,N-dialkylcarbamato ligands display several coordination modes depending on the type of the metal center and its oxidation state.20 Additionally, an intermetallic ligand exchange between a transition metal complex and an organoaluminium co-catalyst can occur resulting in the formation of a variety of new catalytic species in the reaction medium. Such exchange reactions are frequently observed in olefin polymerization reactions.33,38–40

For example, some of us reported that a treatment of Nb(O2CNEt2)5 with Et3Al2Cl3 at a 1:1 molar ratio resulted in the formation of the [Al2(O2CNEt2)2Et2]Cl complex. Observation of such complexes indicates that an interaction of homoleptic carbamate complexes with organoaluminium co-catalysts in the course of a polymerization reaction may proceed via the transfer of the carbamate ligands from the former to the latter.41

The catalyst systems derived from complexes I–III and utilizing MAO as a co-catalyst (Table 2) also contain several types of active centers. Run 15 was carried out with the III–MAO system under approximately the same conditions as those in run 3 where the Et3Al2Cl3/Al′Bu3 co-catalyst was used. Both the copolymers have significant similarities in terms of their molecular weight distribution. The dominant Flory component V in the product formed in run 15 (ca 80%) also has a very high $M_n^{av}$ of ca 9 × 10^5. However, this copolymer has a much higher average $C_{Hex}^{copol}$ value, 11 mol% versus ca 2 mol% in run 3. The $r_1$ reactivity ratio for this center (estimated with Eqn (2)) in the III–MAO system is ca 20, which means that the dominant active center in this catalyst copolymerizes 1-hexene with ethylene about 10 times better.

When $r_2$ in a copolymerization reaction with the III–MAO catalyst was decreased 10 times (run 10), the catalyst productivity decreased approximately six times. The distribution of Flory components (Table 3) changed similarly to that observed in the comparison of run 3 and run 1: the fraction of Flory component V (the component with the highest $M_n$) strongly decreased (its $M_n^{av}$ decreased as well) and several Flory components with low $M_n$ dominated the molecular weight distribution. The microstructure of the E/H copolymers prepared with carbamate Ti complexes was investigated by 13C NMR. General features of such copolymer spectra have already been reported in the literature.28,42–44 A typical 13C NMR spectrum (product from run 8, produced with the I–Et3Al2Cl3/Al′Bu3 catalyst) is shown in Fig. 5; Scheme 2 gives the nomenclature of carbon atoms in a typical EEEHEE sequence.

Table 4. 13C NMR data: 1-hexene mole fractions, average sequence lengths and triad distribution

<table>
<thead>
<tr>
<th>Run</th>
<th>$C_{Hex}^{copol}$</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>[EHE]</th>
<th>[EHH]</th>
<th>[HHH]</th>
<th>[HEH]</th>
<th>[HEE]</th>
<th>[EEE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>1.8</td>
<td>4.5</td>
<td>0.07</td>
<td>0.18</td>
<td>0.03</td>
<td>0.08</td>
<td>0.16</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>1.0</td>
<td>15.7</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.12</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>0.26</td>
<td>2.1</td>
<td>5.9</td>
<td>0.10</td>
<td>0.05</td>
<td>0.11</td>
<td>0.08</td>
<td>0.09</td>
<td>0.57</td>
</tr>
<tr>
<td>10</td>
<td>0.17</td>
<td>1.3</td>
<td>6.4</td>
<td>0.11</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.20</td>
<td>0.60</td>
</tr>
<tr>
<td>11</td>
<td>0.16</td>
<td>1.3</td>
<td>6.7</td>
<td>0.12</td>
<td>0.04</td>
<td>0.00</td>
<td>0.04</td>
<td>0.17</td>
<td>0.63</td>
</tr>
</tbody>
</table>

* H, 1-hexene; E, ethylene.

Fig. 5: Scheme 2 gives the nomenclature of carbon atoms in a typical EEEHEE sequence.

The relative amounts of triad sequences were calculated for several copolymer samples following Hsieh and Randall28 and were verified by using areas of individual peaks determined by spectral deconvolution. The results are tabulated in Table 4. Average sequence lengths for ethylene ($\bar{M}_n$) and 1-hexene ($\bar{M}_w$) in Table 4, given by the ratio of the monomer mole fraction and 1-hexene runs per average molecule, $N/[N] = 0.5[HE]$, were obtained from the triad sequence composition. The results demonstrate that all the materials prepared with catalysts based on carbamato Ti complexes are real copolymers and mostly contain isolated 1-hexene units (HEE and EHE triads, low $\bar{M}_n$ values) separated by relatively long ethylene sequences (high $\bar{M}_w$ values).

An unusual feature of the copolymer produced in run 8 with the I–Et3Al2Cl3/Al′Bu3 catalyst is a disproportionately large fraction of long 1-hexene sequences, which is obvious both from Table 4 and Fig. 5. For example, a compositionally uniform copolymer containing 26 mol% of 1-hexene can be expected32 to have an [HHH]/[HEE]:[EEE] ratio of ca 2.5:7:8 (the expectedly measured ratio is 1.0:45.9:0.91). This difference represents another manifestation of the multi-center nature of this catalyst. The molecular weight distribution of the polymer formed in run 8 is very broad ($M_n/M_w = 24.5$); some active centers in the catalyst copolymerize 1-hexene with ethylene very well and form copolymer fractions with $C_{Hex}^{copol}$ values >50–60 mol% containing a small amount of [HHH]$_n$ blocks.

**CONCLUSIONS**

Three post-metallocene polymerization catalysts based on Ti(IV) complexes with bidentate N,N-dialkylcarbamato ligands, I–III, were employed as catalyst precursors in E/H copolymerization reactions in the presence of two different organoaluminium cocatalysts, Et3Al2Cl3/Al′Bu3 and MAO. All the catalyst systems were active in the copolymerization reactions and produced copolymers with high 1-hexene contents. Complex III activated...
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REFERENCES

Post-metallocene catalyst for alkene polymerization www.soci.org