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2. $^1$H NMR spectra for Ni1 – Ni10

**Figure S17.** $^1$H NMR spectrum of Ni1 in CD$_2$Cl$_2$ at room temperature

**Figure S18.** $^1$H NMR spectrum of Ni2 in CD$_2$Cl$_2$ at room temperature
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3. $^1$H NMR spectra for [1,2-(ArN)$_2$C$_2$C$_{10}$H$_6$]NiBr$_2$ (Ar = 2,6-Me$_2$C$_6$H$_3$, $^1$ 2,6-Et$_2$C$_6$H$_3$, $^2$ 2,6-iPr$_2$C$_6$H$_3$, $^1$, $^3$ 2,4,6-Me$_3$C$_6$H$_2$, $^4$)

Figure S27. $^1$H NMR spectrum of [1,2-(2,6-Me$_2$C$_6$H$_3$N)$_2$C$_2$C$_{10}$H$_6$]NiBr$_2$ (C1) in CD$_2$Cl$_2$ at room temperature

Figure S28. $^1$H NMR spectrum of [1,2-(2,6-Et$_2$C$_6$H$_3$N)$_2$C$_2$C$_{10}$H$_6$]NiBr$_2$ (C2) in CD$_2$Cl$_2$ at room temperature
**Figure S29.** $^1$H NMR spectrum of $[1,2-(2,6-iPr_2C_6H_3N)_2C_2C_{10}H_6]NiBr_2$ (C3) in CD$_2$Cl$_2$ at room temperature (the peak for the Ar-o-CH proton was not visible)

**Figure S30.** $^1$H NMR spectrum of $[1,2-(2,4,6-Me_3C_6H_2N)_2C_2C_{10}H_6]NiBr_2$ (C4) in CD$_2$Cl$_2$ at room temperature
4. $^{19}$F NMR spectra for Ni1 – Ni10

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5. $^{19}$F NMR spectra for the species formed on treating Ni2 with 10, 50 and 100 equivalents of EASC

![Figure S41. $^{19}$F NMR spectra of Ni2/EASC with different Al/Ni ratios. At a ratio of Al/Ni2 = 50, two species a and b have been identified](image)

6. Polyethylene microstructures

**Table S1.** Carbon-13 NMR: Chemical shift, integral and assignments of the polyethylenes obtained using Ni4/EASC (entry 4 in Table 4)

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Chem. Shift (ppm)</th>
<th>Integral</th>
<th>Assignments</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>11.29</td>
<td>0.21</td>
<td>1B$_2^{-}$I$_1$</td>
</tr>
<tr>
<td>2</td>
<td>14.28</td>
<td>0.44</td>
<td>1B$_4^{-}$I$_2$</td>
</tr>
<tr>
<td>3</td>
<td>20.11</td>
<td>1</td>
<td>1B$_1^{-}$I$_4$</td>
</tr>
<tr>
<td>4</td>
<td>22.91</td>
<td>0.39</td>
<td>2B$_n^{-}$I$_7$</td>
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<tr>
<td>5</td>
<td>26.79</td>
<td>0.35</td>
<td>2B$<em>2^{-}$I$</em>{10}$</td>
</tr>
<tr>
<td>6</td>
<td>27.25</td>
<td>0.88</td>
<td>$\beta$B$<em>2^{-}$I$</em>{11}$; (n-1)B$<em>n^{-}$I$</em>{11}$</td>
</tr>
<tr>
<td>7</td>
<td>27.44</td>
<td>0.86</td>
<td>$\beta$B$<em>1^{-}$I$</em>{12}$</td>
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</tbody>
</table>
### Table S2. Carbon-13 NMR: Chemical shift, integral and assignments of the polyethylene obtained using Ni6/EASC (entry 3 in Table 5)

<table>
<thead>
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<th>Peak No.</th>
<th>Chem. Shift (ppm)</th>
<th>Integral</th>
<th>Assignments</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>0.06</td>
<td>1B\textsubscript{-} I\textsubscript{1}</td>
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<tr>
<td>2</td>
<td>14.25</td>
<td>0.3</td>
<td>1B\textsubscript{4} - I\textsubscript{2}</td>
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<tr>
<td>3</td>
<td>14.73</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20.12</td>
<td>1</td>
<td>1B\textsubscript{1} - I\textsubscript{4}</td>
</tr>
<tr>
<td>5</td>
<td>22.92</td>
<td>0.26</td>
<td>2B\textsubscript{n} - I\textsubscript{7}</td>
</tr>
<tr>
<td>6</td>
<td>26.73</td>
<td>0.15</td>
<td>2B\textsubscript{2} - I\textsubscript{10}</td>
</tr>
<tr>
<td>7</td>
<td>27.28</td>
<td>1.08</td>
<td>βB\textsubscript{1} - I\textsubscript{11}; (n-1)B\textsubscript{n} - I\textsubscript{11}</td>
</tr>
<tr>
<td>8</td>
<td>27.44</td>
<td>1.62</td>
<td>βB\textsubscript{1} - I\textsubscript{12}</td>
</tr>
<tr>
<td>9</td>
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<td>0.64</td>
<td>4B\textsubscript{n} - I\textsubscript{15}</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>10.59</td>
<td>δB\textsubscript{1-a} - I\textsubscript{16}</td>
</tr>
<tr>
<td>11</td>
<td>30.4</td>
<td>2.61</td>
<td>γB\textsubscript{1} - I\textsubscript{17}</td>
</tr>
<tr>
<td>12</td>
<td>32.24</td>
<td>0.29</td>
<td>3B\textsubscript{n} - I\textsubscript{20}</td>
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<tr>
<td>13</td>
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<td>0.82</td>
<td>brB\textsubscript{1} - I\textsubscript{22}</td>
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<tr>
<td>14</td>
<td>34.12</td>
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<td>αB\textsubscript{2} - I\textsubscript{24}</td>
</tr>
<tr>
<td>15</td>
<td>34.53</td>
<td>1.11</td>
<td>n-B\textsubscript{n} - I\textsubscript{26}</td>
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<tr>
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<td>17</td>
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<td>0.35</td>
<td>brB\textsubscript{n} - I\textsubscript{31}</td>
</tr>
</tbody>
</table>

Based on assignments listed in the literature,\textsuperscript{5} the branching content of the polyethylenes could be calculated using the following equations:

\[ N_E = \left( I_{10} + I_{24}/2 + I_{33} \right)/3 \]

\[ N_B = \left( I_8 + I_{25} \right)/2 \]

\[ N_A = I_{21} \]

\[ N_{M(1,4)} = \left( I_{23}/2 + I_{27}/2 \right)/2 \]
\[ N_{L(1,4)} = \left( \frac{I_{19}}{2} + \frac{I_{32}}{2} \right) / 2 \]

\[ N_L = I_{20} - \left( \frac{I_{123}}{2} + \frac{I_{27}}{2} \right) \]

\[ N_M = I_{12} - \left( \frac{I_{123}}{2} + \frac{I_{27}}{2} + \frac{I_{13}}{1} + \frac{I_{21}}{1} + 2I_9 \right) / 2 \]

Total methyl branches = \( N_M + N_{M(1,4)} + N_{M(1,5)} + N_{M(1,6)} \)

Total longer chain branches = \( N_L + N_{L(1,4)} \)

The polyethylene produced using \( \text{Ni}^4/\text{EASC} \) possessed 85 branches per 1000 carbons including methyl (56.6%), ethyl (23.3%) and longer chains (20.1%). By contrast, the polyethylene obtained using \( \text{Ni}^6/\text{EASC} \) contained 116 branches per 1000 carbons, including methyl (52.6%), ethyl (6.4%) and longer chains (41.0%).

7. References