Preparation of Polyethylenes End-Tethered with POSS

**Preparation of complex**

\[
\begin{align*}
\text{SbF}_6^- + \text{MeCN} &\rightarrow + \text{MeCN} \\
\text{Pd}^{\text{II}} - \text{diimine} &\rightarrow \text{Pd}^{\text{II}} - \text{diimine} + \text{SbF}_6^- \\
\text{CH}_2\text{Cl}_2 &\rightarrow \text{Et}_2\text{O} \\
\text{Et}_3\text{SiH} &\rightarrow \text{MeCN} \\
\text{POSS} &\rightarrow \text{POSS} + \text{MeCN}
\end{align*}
\]

**Ethylene polymerization**

\[
\begin{align*}
\text{SbF}_6^- &\rightarrow \text{SbF}_6^- \\
\text{Pd}^{\text{II}} - \text{diimine} &\rightarrow \text{Pd}^{\text{II}} - \text{diimine} + \text{SbF}_6^- \\
\text{PhCl} &\rightarrow + \text{Et}_3\text{SiH} \\
\text{POSS} &\rightarrow \text{POSS} + \text{Et}_3\text{SiH}
\end{align*}
\]

**Monitoring results of 5**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mn, GPC (kg/mol)</th>
<th>PDI, GPC</th>
<th>Mn, NMR (kg/mol)</th>
<th>Branches (per 1000C)</th>
<th>Time (h)</th>
<th>Mn, GPC (kg/mol)</th>
<th>PDI, GPC</th>
<th>Mn, NMR (kg/mol)</th>
<th>Branches (per 1000C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.2</td>
<td>1.11</td>
<td>11.2</td>
<td>89</td>
<td>4</td>
<td>43.5</td>
<td>1.12</td>
<td>36.3</td>
<td>87</td>
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<td>2</td>
<td>24.4</td>
<td>1.17</td>
<td>19.1</td>
<td>88</td>
<td>5</td>
<td>52.4</td>
<td>1.19</td>
<td>45.9</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>36.6</td>
<td>1.14</td>
<td>29.6</td>
<td>88</td>
<td>6</td>
<td>56.4</td>
<td>1.17</td>
<td>51.6</td>
<td>87</td>
</tr>
</tbody>
</table>

**Significance:** Preparation of a homogeneous polyhedral silsesquioxane (POSS)-supported Pd–diimine complex 3 and telechelic polyethylenes end-tethered with POSS nanoparticles 5 was reported. Thus, complex 3 was prepared by the reaction of a Pd–diimine catalyst 1 with acryloisobutyl-POSS 2 at room temperature for 48 h (40% yield). Ethylene polymerization was carried out with 3 at 5 °C under 27.5 bar in chlorobenzene followed by quenching 4 with triethylsilane to afford compound 5.

**Comment:** Monitoring results of 5 led to the following conclusions: The number average molecular weight (Mn) was increased in proportion to time (1 h; 15.2 kg/mol vs 6 h; 56.4 kg/mol). The polydispersity index (PDI) value was within 1.11–1.19. \(^1\)H NMR measurements exhibited that these polymers were branched with ca. 88 branches per 1000 carbons.

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