Supporting Information

One-pot syntheses of heterotelechelic α-vinyl,ω-methoxysilane polyethylenes and condensation into comb-like and star-like polymers with high chain end functionality.

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Figure S1. ¹H NMR spectrum of alkoxysilyl-PE isolated after deactivation with a amount of TMOS (Si/Mg = 0.5) of PE-Mg-PE chains obtained by CCG using [(C₅Me₅)₂NdCl₂Li(OEt₂)₂]/BOMAG catalytic system

³H NMR (TCE/C₆D₆ 2/1, 400 MHz, 363 K) δ ppm: 0.57 (c), 0.84 (a), 1.26 (b), 1.97 (Vt), 3.41 (d), 4.89 (Vt), 5.74 (Vt)

Determination of the number of PE chains per silicon atom:

Number of PE per silicon atom = 4(1-CH₂-Si/2) / (1-CH₂-Si/2 + 1-SiOCH₃/3) = 2.36

Number of corresponding methoxysilane group = 4(1-SiOCH₃/3) / (1-CH₂-Si/2 + 1-SiOCH₃/3) = 1.64
Figure S2. $^{13}$C NMR spectrum alkoxyisilyl-PE isolated after deactivation with TMOS (Si/Mg = 0.5) of PE-Mg-PE chains obtained by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt)_2]$/BOMAG catalytic system

$^{13}$C NMR (TCE/$C_6D_6$ 2/1, 100 MHz, 363 K) $\delta$ ppm: 12.78 (e), 14.08 (1s), 22.95 (2s), 23.15 (d), 29.66 (4s), 29.71 (b), 30.06 (a), 32.26 (3s), 33.65 (c), 50.01 (f)
Alkoxysilyl-PE isolated after deactivation with an excess amount of functionalizing agent (Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using [(CsMe$_3$)$_2$NdCl$_2$Li(OEt)$_2$/di(10-undecenyl)magnesium catalytic system.

Table S1. Determination of the number of PE chains per silicon atom

<table>
<thead>
<tr>
<th></th>
<th>I-CH$_2$-Si</th>
<th>I-SiOCH$_3$</th>
<th>Number of PE per silicon atom</th>
<th>Number of corresponding methoxysilane group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vin-PE-DMMS</td>
<td>1.63</td>
<td>4.54</td>
<td>1.05</td>
<td>1.95</td>
</tr>
<tr>
<td>Vin-PE-DMVS</td>
<td>1.81</td>
<td>4.67</td>
<td>1.10</td>
<td>1.90</td>
</tr>
<tr>
<td>Vin-PE-TMS</td>
<td>1.5</td>
<td>6.51</td>
<td>1.03</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Number of PE per silicon atom = $x$*(I-CH$_2$-Si/2) / ((I-CH$_2$-Si/2) + (I-SiOCH$_3$/3))

Number of corresponding methoxysilane group = $x$*(I-SiOCH$_3$/3) / ( (I-CH$_2$-Si/ 2) + (I-SiOCH$_3$/3))

$x$=3 for Vin-PE-DMMS, Vin-PE-DMVS and $x$=4 for Vin-PE-TMS
Figure S3. $^{13}$C NMR spectrum of Vin-PE-DMMS isolated after deactivation with an excess amount of TMMS (diluted in dried toluene, Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using [((C$_5$Mes)$_2$NdCl$_2$Li(OEt)$_2$]/di(10-undecenyl)magnesium catalytic system

$^{13}$C NMR (TCE/C$_6$D$_6$ 2/1, 100 MHz, 363 K) δ ppm: -5.51 (m), 13.82 (k), 23.12 (j), 29.38 (f), 29.50 (e), 29.70 (h), 29.86 (d), 30.06 (g), 33.49 (i), 34.04 (c), 49.80 (l), 114.25 (a), 138.96 (b)
Figure S4. $^{13}$C NMR spectrum of Vin-PE-DMVS isolated after deactivation with an excess amount of TMVS (diluted in dried toluene, Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt)_2]/di(10$-undecenyl)magnesium catalytic system

$^{13}$C NMR (TCE/C$_6$D$_6$ 2/1, 100 MHz, 363 K) δ ppm: 12.75 (k), 22.92 (j), 29.38 (i), 29.49 (e), 29.67 (h), 29.85 (d), 30.06 (g), 33.47 (i), 34.04 (c), 50.15 (l), 114.25 (a), 133.23 (n), 134.89 (m), 138.98 (b)
Figure S5. $^{13}$C NMR spectrum of Vin-PE-TMS isolated after deactivation with an excess amount of TMOS (Si/Mg = 10) of PE-Mg-PE chains obtained by CCG using $[(C_{5}Me_{5})_{2}NdCl_{2}Li(OEt)_{2}]/$di(10-undecenyl)magnesium catalytic system.

$^{13}$C NMR (TCE/C$_{6}$D$_{6}$ 2/1, 100 MHz, 363 K) δ ppm: 9.86 (k), 23.04 (j), 29.38 (f), 29.49 (e), 29.66 (h), 29.85 (d), 30.06 (g), 33.31 (i), 34.03 (c), 50.15 (l), 114.25 (a), 138.98 (b)
Figure S6. HT-SEC (150°C in TCB) of Vin-PE-DMMS. The two samples have been respectively left for solubilization during 15 min and 5h in TCB at 150°C before HT SEC analysis.
Figure S7. A) MALDI-TOF MS analysis of Vin-PE-DMMS in the reflectron mode using dithranol as matrix and B) simulation of the isotopic distribution using ISOPRO software.

\[ m/z \, 1962.8 = 105.04 + (n \times 28.03) + 41.04 + 23, \, n = 64, \text{ formula of the polymer: } C_{128}H_{256} + C_6H_{14}O_2SiNa \]

Isopro simulation: \( C_{134} H_{270} O_2 Na_i Si_i \)
Figure S8. A) MALDI-TOF MS analysis of Vin-PE-DMVS in the reflectron mode using dithranol as matrix and B) simulation of the isotopic distribution using ISOPRO software

\[ m/z \ 1358.3 = 117.04 + (n \times 28.03) + 41.04 + 23, \ n = 42, \ \text{formula of the polymer:} \ C_{84}H_{168} + C_{7}H_{14}O_2SiNa \]

Isopro simulation: \( C_{91}H_{182}O_2Na_1Si_1 \)
Scheme S1. Mechanism involved in the hydrolysis-condensation of alkoxyisilyl-PE$^1$
Figure S9. $^1$H NMR spectra of a) Vin-PE-DMMS, b) comb-Vin-PE-DMMS (20 eq) and c) comb-Vin-PE-DMMS (40 eq)

Figure S10. $^{13}$C NMR spectrum of comb-Vin-PE-DMMS, * corresponds to carbons adjacent to the silicon atom
Figure S11. $^{13}$C NMR spectrum of star-Vin-PE-TMS, * corresponds to carbons adjacent to the silicon atom.
Figure S12. $^1$H-$^{13}$C HSQC of star-Vin-PE-TMS
Figure S13. Mark-Houwink plots of Vin-PE-DMMS (filled squares), comb-Vin-PE-DMMS (open squares), Vin-PE-TMS (filled circles) and star-Vin-PE-TMS (open circles) obtained using the Mark-Houwink relation: \( \log[\eta] = \log(k) + \alpha \log M \)

Reference