Supplementary Information: Alkoxysilyl Functionalized Polynorbornenes with Enhanced Selectivity for Heavy Hydrocarbon Separations

Synthesis of the trimethylsilyl norbornene monomer

Under nitrogen, a 100-mL Schlenk flask was charged with cyclopentadiene (4.75 ml, 35.2 mmol) and vinyltrimethyl silane (31 mL, 211.6 mmol), heated to 205 ℃, and stirred for 3 hours. After 3 hours, the reaction mixture was cooled to room temperature before it was distilled and isolated as a clear liquid at 74% yield.

![Diels-Alder reaction](image)

**Figure S1.** Cracking of dicyclopentadiene and subsequent Diels-Alder reaction with vinyl trimethylsilane

Viscosity testing of low molecular weight addition-type oligomers produced from nickel catalysis

Inherent viscosity results of addition-type polymers prepared from nickel naphthenate (Nph) catalyst conditions. Viscosity testing performed using 1.0 g/dL solution in toluene at 35 ℃.

![Viscosity vs Concentration](image)

**Figure S2.** Nickel catalysts gave low inherent viscosities in toluene for several monomer and catalyst concentrations
Gel permeation chromatography (GPC) of ROMP-SiMe₃ and GPC of APN-SiMe₃ synthesized from nickel (Ni) catalyst and palladium (Pd) catalyst

Table S1. GPC confirmed that nickel naphthenate produced molecular weight species of insufficient molecular weight for film formation

<table>
<thead>
<tr>
<th>30 °C</th>
<th>APN-SiMe₃ [Ni(nph)₂ catalyst]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mₙ</td>
</tr>
<tr>
<td></td>
<td>Mₚ</td>
</tr>
<tr>
<td></td>
<td>M₂</td>
</tr>
<tr>
<td></td>
<td>Mₚ</td>
</tr>
<tr>
<td></td>
<td>Mₚ/Mₙ</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>0.1589</td>
</tr>
<tr>
<td>Sample Recovery (%)</td>
<td>99.26</td>
</tr>
<tr>
<td>dn/dc</td>
<td>2.738</td>
</tr>
</tbody>
</table>

Table S2. GPC results for high molecular polymers used for film casting

<table>
<thead>
<tr>
<th>30 °C</th>
<th>ROMP-SiMe₃</th>
<th>APN-SiMe₃ (Pd catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mₙ</td>
<td>60194</td>
</tr>
<tr>
<td></td>
<td>Mₚ</td>
<td>102180</td>
</tr>
<tr>
<td></td>
<td>M₂</td>
<td>236270</td>
</tr>
<tr>
<td></td>
<td>Mₚ</td>
<td>80227</td>
</tr>
<tr>
<td></td>
<td>Mₚ/Mₙ</td>
<td>1.698</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>0.5506</td>
<td>0.3387</td>
</tr>
<tr>
<td>Sample Recovery (%)</td>
<td>99.673</td>
<td>106.35</td>
</tr>
<tr>
<td>dn/dc</td>
<td>0.0373</td>
<td>0.0405</td>
</tr>
</tbody>
</table>
Thermogravimetric analysis showed high thermal stability of the synthesized polymers.

Figure S3. Thermal stability comparison of the ROMP polymers.
Figure S4. Thermal stability comparison of the addition-type polymers
Infrared spectroscopy of the synthesized polymers

**Figure S5.** ATR-FTIR shows varying ethoxysilyl and methylsilyl content in the ROMP polymers
Figure S6. ATR-FTIR shows varying ethoxysilyl and methylsilyl content in the addition-type polymers.
Dynamic mechanical analysis probed glass transition temperatures of synthesized polymers

**Figure S7.** Glass transition temperatures of ROMP polymers from Tan (delta) peaks
Figure S8. Glass transition temperatures of addition-type polymers from Tan (delta) peaks
$^1$H-NMR and $^{13}$C-NMR spectroscopy of monomers and $^1$H-NMR of polymers with appropriate integrations and peak designations

Figure S9. $^1$H-NMR with appropriate peak positions and integrations for trimethylsilyl norbornene

NMR spectra are in agreement with the formation of trimethylsilyl norbornene.

$^1$H NMR (CDCl$_3$): δ 6.16 (dd, 1H, minor), 5.95 (dd, 1H, minor), 5.93 (dd, 1H, major), 5.92 (dd, 1H, major), 2.93 (br s, 1H, major), 2.91 (br s, 1H, minor), 2.87 (br s, 1H, major), 2.73 (br s, 1H, minor), 1.85 (ddd, 1H, major), 1.52 (ddd, 1H, major), 1.38 (ddd, 1H, major), 1.16 (m, 1H, minor), 1.15 (m, 1H, major), 1.13 (m, 1H, minor), 1.12 (m, 1H, major), 1.05 (m, 1H, minor), 1.03 (m, 1H, major), 0.92 (ddd, 1H, major), 0.31 (ddd, 1H, minor), 0.00 (s, 3H, minor), -0.10 (s, 3H, major)
Figure S10. $^{13}$C-NMR with appropriate peak positions for trimethylsilyl norbornene
NMR spectra for dimethylethoxysilyl norbornene:

$^1$H NMR (CDCl$_3$): $\delta$ 6.15 (dd, 1H, minor), 5.98 (dd, 1H, major), 5.94 (dd, 1H, major), 5.92 (dd, 1H, minor), 3.68 (q, 2H, minor), 3.65 (q, 2H, major), 2.97 (br s, 1H, major), 2.92 (br s, 1H, minor), 2.88 (br s, 1H, major), 2.81 (br s, 1H, minor), 1.88 (ddd, 1H, major), 1.62 (ddd, 1H, minor), 1.38 (ddd, 1H, major), 1.19 (t, 3H, minor), 1.18 (t, 3H, major), 1.17 (m, 1H, minor), 1.16 (m, 1H, major), 1.13 (m, 1H, major), 1.12 (m, 1H, major), 1.05 (m, 1H, minor), 1.03 (m, 1H, minor), 1.00 (ddd, 1H, major), 0.41 (ddd, 1H, minor), 0.12 (s, 3H, minor), 0.11 (s, 3H, minor), 0.04 (s, 3H, major), -0.04 (s, 3H, major)
Figure S12. $^{13}$C-NMR with appropriate peak positions for dimethylethoxysilyl norbornene
Figure S13. $^1$H-NMR with appropriate peak positions and integrations for methyldiethoxysilyl norbornene

NMR spectra for methyldiethoxysilyl norbornene:

$^1$H NMR (CDCl$_3$): δ 6.13 (dd, 1H, major), 5.98 (m, 2H, minor), 5.91 (dd, 1H, major), 3.78 (q, 2H, major), 3.78 (q, 2H, major), 3.76 (q, 2H, minor), 3.72 (q, 2H, minor), 3.00 (m, 1H, minor), 2.92 (br s, 1H, major), 2.88 (m, 1H, minor), 2.86 (br s, 1H, major), 1.88 (ddd, 1H, minor), 1.70 (ddd, 1H, major), 1.38 (m, 1H, minor), 1.36 (m, 1H, major), 1.22 (t, 3H, major), 1.21 (t, 3H, major), 1.20 (t, 3H, minor), 1.18 (t, 3H, minor), 1.17 (m, 1H, major), 1.15 (m, 1H, minor), 1.11 (m, 1H, minor), 1.09 (m, 1H, major), 1.05 (ddd, 1H, minor), 0.45 (ddd, 1H, major), 0.13 (s, 3H, major), -0.04 (s, 3H, minor)
Figure S14. $^{13}$C-NMR with appropriate peak positions for methyldiethoxysilyl norbornene
Figure S15. $^1$H-NMR with appropriate peak positions and integrations for triethoxysilyl norbornene

NMR spectra for triethoxysilyl norbornene:

$^1$H NMR (CDCl$_3$): $\delta$ 6.12 (dd, 1H, major), 6.01 (m, 2H, minor), 5.91 (dd, 1H, major), 3.83 (q, 6H, major), 3.77 (q, 6H, minor), 3.02 (m, 1H, minor), 2.92 (br s, 1H, major), 2.91 (br s, 1H, major), 2.87 (br s, 1H, minor), 1.86 (ddd, 1H, minor), 1.77 (ddd, 1H, major), 1.37 (m, 1H, minor), 1.35 (m, 1H, major), 1.35 (br s, 1H, minor), 1.33 (br s, 1H, major), 1.22 (t, 9H, major), 1.19 (t, 9H, minor), 1.17 (m, 1H, major), 1.15 (m, 1H, minor), 1.08 (m, 1H, minor), 0.45 (ddd, 1H, major)
Figure S16. $^{13}$C-NMR with appropriate peak positions for triethoxysilyl norbornene
Figure S17. $^1$H-NMR with appropriate peak positions and integrations for ROMP-SiMe$_3$.

NMR spectra are in agreement with the formation of ROMP-SiMe$_3$.

$^1$H NMR (CDCl$_3$): $\delta$ 5.25 (several broad peaks, 2H, alkenyl), 3.32-0.63 (several broad peaks, aliphatic, 7H), 0.00 and -0.04 (singlets, -Si(CH$_3$)$_3$, 9H)
Figure S18. $^1$H-NMR with appropriate peak positions and integrations for ROMP-SiMe$_2$OEt

NMR spectra are in agreement with the formation of ROMP-SiMe$_2$OEt.

$^1$H NMR (CDCl$_3$): $\delta$ 5.26 (several broad peaks, 2H, alkenyl), 3.36 (br s, Si(OCH$_2$CH$_3$), 2H) 3.32-1.42 (several broad peaks, aliphatic, 5H + H$_2$O), 1.30 (br s, aliphatic, 1H), 1.17 (s, Si(OCH$_2$CH$_3$), 3H), 0.16 (br shoulder, aliphatic, 1H), 0.10 and 0.06 (singlets, -Si(CH$_3$)$_3$, 6H)
Figure S19. $^1$H-NMR with appropriate peak positions and integrations for ROMP-SiMe(OEt)$_2$.

NMR spectra are in agreement with the formation of ROMP-SiMe(OEt)$_2$.

$^1$H NMR (CDCl$_3$): $\delta$ 5.28 (several broad peaks, 2H, alkenyl), 3.73 (br s, Si(OCH$_2$CH$_3$), 4H) 3.27-1.27 (several broad peaks, aliphatic, 6H + H$_2$O), 1.19 (s, Si(OCH$_2$CH$_3$), 6H), 0.16 (br shoulder, aliphatic, 1H), 0.13/0.10 and 0.06 (singlets, -Si(CH$_3$)$_3$, 3H)
NMR spectra are in agreement with the formation of ROMP-Si(OEt)$_3$.

$^1$H NMR (CDCl$_3$): $\delta$ 5.34 (several broad peaks, 2H, alkenyl), 3.80 (br s, Si(OCH$_2$CH$_3$), 6H) 3.27-1.30 (several broad peaks, aliphatic, 6H + H$_2$O), 1.20 (s, Si(OCH$_2$CH$_3$), 9H), 0.16 (br shoulder, aliphatic, 1H)
NMR spectra are in agreement with the formation of APN-SiMe₃.

$^1$H NMR (CDCl₃): $\delta$ 3.24-0.25 (several broad peaks, aliphatic, 9H), 0.04 and -0.04 (singlets, -Si(CH₃)₃, 9H)
NMR spectra are in agreement with the formation of APN-SiMe₂OEt.

\(^1\text{H NMR (CDCl}_3\): \(\delta\) 3.64 (br s, Si(OCH₂CH₃), 2H), 1.14 (br s, Si(OCH₂CH₃), 3H), 3.28-0.35 (several broad peaks, aliphatic, 9H), 0.06 (br s, -Si(CH₃)₃, 6H)
NMR spectra are in agreement with the formation of APN-SiMe(OEt)$_2$.

$^1$H NMR (CDCl$_3$): $\delta$ 3.74 (br s, Si(OCH$_2$CH$_3$), 4H), 1.17 (br s, Si(OCH$_2$CH$_3$), 6H), 3.46-0.35 (several broad peaks, aliphatic, 9H), 0.07 (br s, -Si(CH$_3$)$_3$, 3H)
Figure S24. $^1$H-NMR with appropriate peak positions and integrations for APN-Si(OEt)$_3$.

NMR spectra are in agreement with the formation of APN-Si(OEt)$_3$.

$^1$H NMR (CDCl$_3$): $\delta$ 3.79 (br s, Si(OCH$_2$CH$_3$), 6H), 1.19 (br s, Si(OCH$_2$CH$_3$), 9H), 3.42-0.16 (several broad peaks, aliphatic, 9H)