Supporting Information

A New Echelon of Precision Polypentenamers: Highly Isotactic Branching on Every Five Carbons

Stefan Brits, William J. Neary, Goutam Palui, & Justin G. Kennemur

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA

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Figure SI-52. DSC overlay of all polymer samples
Mosher acid synthesis for the determination of % enantiomeric excess:

To a flame dried 4mL vial equipped with a stir bar, 7.1 mg (84.4 µmol, 1 eq.) of (S)-1 and 1.00 mL of DCM that was previously run through a plug of silica gel were added. To a separate dry vial, 0.0613 g (261.6 µmol, 3.1 eq.) of (R)-(+)−α-methoxy-α-trifluoromethylphenylacetic was added and dissolved in 0.32 mL of DCM. This solution was then added to (S)-1. To the solution, 0.0545g (261.4 µmol, 3.1 eq.) of DCC and 0.0323g (261.4 µmol, 3.1 eq.) of DMAP were added and capped. The mixture was allowed to stir for 3 hours. At this time, the mixture was run through a cotton plug and concentrated. The mixture was purified with a pipet column in 4:1 hexanes:EtoAc. The product was then concentrated and placed on the high-vacuum for 30 minutes. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.51 (m, 2H), 7.40 (m, 3H), 6.15 (ddd, J = 5.7, 2.6, 1.6 Hz, 1H), 5.92 (m, 1H), 5.86 (m, 1H), 3.55 (s, 1H), 2.50 (dtdd, J = 15.8, 8.9, 4.2, 2.4 Hz, 1H), 2.37 (m, 2H), 1.95 (m, 1H)

(R, R)-DACH Phenyl Trost ligand:

The Trost ligand was synthesized following previous literature with the following modifications. The brown solid was purified with 97.5:2.5 DCM:MeOH via column chromatography and recrystallized twice from MeCN to yield a white solid. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.60 – 7.55 (m, 2H), 7.35 – 7.17 (m, 24H), 6.94 – 6.88 (m, 2H), 6.32 (d, J = 6.9 Hz, 2H), 3.82 – 3.73 (m, 2H), 1.90 – 1.82 (m, 2H), 1.69 – 1.61 (m, 2H), 1.28 – 1.15 (m, 2H), 0.98 (td, J = 15.1, 13.8, 6.2 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 169.29, 140.88, 140.72, 137.84, 137.76, 137.70, 136.73, 136.58, 134.27, 133.95, 133.82, 130.16, 128.75, 128.60, 128.54, 128.51, 128.49, 128.45, 128.40, 53.89, 32.00, 24.66. ³¹P NMR (243 MHz, CDCl₃) δ -9.78.
Figure S1. $^1$H-NMR spectrum of rac-1, (in $^*\text{CDCl}_3$ 400 MHz)
Figure S2. $^{13}$C-NMR spectrum of rac-1, (in $^*$CDCl$_3$ 150 MHz)
Figure S3. $^1$H-$^1$H COSY spectrum of rac-1, (in CDCl$_3$ 600 MHz)
Figure S4. The mass spectrum at RT 4.08-4.12 min for rac-1. The molecular peak is observed at \( m/z \) 84.07.
**Figure S5.** $^1$H-NMR spectrum of rac-3, (in *CDCl$_3$ 500 MHz).
Figure S6. $^{13}$C-NMR spectrum of rac-3, (in $^\text{CDCl}_3$ 150 MHz)
Figure S7. $^1$H-$^1$H COSY spectrum of rac-3, (in CDCl$_3$ 500 MHz).
Figure S8: The mass spectrum at RT 8.27-8.32 min for the sample rac-3 The molecular peak is observed at m/z 198.15.
Figure S9. $^1$H-NMR spectrum of rac-2, (in $^{*}$CDCl$_3$ 400 MHz)
Figure S10. $^{13}$C-NMR spectrum of rac-2, (in $^{*}$CDCl$_3$ 150 MHz)
**Figure S11.** $^1$H-$^1$H COSY spectrum of rac-2, (in CDCl$_3$ 600 MHz)
**Figure S12.** The mass spectrum at RT 5.60-5.65 min for the sample *rac*-2. The molecular peak is observed at *m/z* 156.10.
Figure S13. $^1$H-NMR spectrum of rac-4, (in $^*$CDCl$_3$ 400 MHz)
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Figure S19: The mass spectrum at RT 4.08-4.12 min for (S)-1. The molecular peak is observed at \( m/z \) 84.06.
Figure S 20. $^1$H-NMR spectrum of (S)-2-MTPACP ester (in $^*\text{CDCl}_3$, 400 MHz).
Figure S21. $^1$H-$^1$H COSY spectrum of (S)-2-MTPACP ester, (in CDCl$_3$, 400 MHz.).
Figure S 22. $^1$H-NMR of (S)-2-MTPACP ester (in CDCl$_3$, 400 MHz.).

\[
\% \text{ee} = \frac{\text{area major}}{(\text{area major} + \text{area min})} \times 100 = 90.1 \% \text{ ee}
\]
Figure S 23. $^{19}$F NMR spectrum of (S)-2-MTPACP ester (in CDCl$_3$, 376.5 MHz.). Deconvolution of the peaks were used to determine the integration of the two peaks.

$$\% \text{ ee} = \frac{\text{area major}}{(\text{area major} + \text{area minor})} \times 100 = 90.4 \% \text{ ee}$$
Figure S 24. $^1$H NMR spectrum of (S)-3 (in $^*$CDCl$_3$, 400 MHz).
Figure S 25. $^{13}$C NMR of (S)-3 (in CDCl3, 100 MHz)
Figure S 26: The mass spectrum at RT 8.27-8.34 min of (S)-3. The molecular peak is observed at m/z 198.16.
Figure S 27. $^1$H NMR spectrum of Trost ligand (in *CDCl$_3$, 600 MHz) # DCM
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Figure S 33. $^1$H-NMR spectrum of Poly[(S)-3] (CDCl$_3$, 400 MHz). Deconvolution of the peaks were used to determine the %HT and % trans of the polymer.

\[
\text{% HT} = \frac{\text{area of cis} - \text{HT} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 91.4 \%
\]

\[
\text{% trans} = \frac{\text{area of trans} - \text{HH} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 95.6 \%
\]
Figure S 34. SEC RI trace of Poly(S)-3. (Đ – 2.81, Mn – 30.2 kDa)
Figure S 35. $^1$H NMR of spectrum of Poly(rac-3), (in *CDCl$_3$, 500 MHz)
Figure S 36. $^{13}$C NMR of spectrum of Poly(rac-3), (in *CDCl$_3$, 150 MHz)
Figure 37. $^1$H-$^1$H COSY of spectrum of Poly(rac-3), (in CDCl$_3$, 500 MHz)
Figure S 38. $^1$H-NMR spectrum of Poly(rac-3) (CDCl$_3$, 400 MHz). Deconvolution of the peaks were used to determine the %HT and % trans of the polymer.

\[
\%HT = \frac{\text{area of cis} - \text{HT} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 92.1 \%.
\]

\[
\%\text{trans} = \frac{\text{area of trans} - \text{HH} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 95.6 \%.
\]
Figure S 39. SEC RI trace of Poly(rac-3). (Đ – 2.56, Mn – 22.3 kDa)
Figure S 40. $^1$H NMR spectrum of Poly(rac-2), (in *CDCl$_3$, 500 MHz)
Figure S 41. $^{13}$C NMR spectrum of Poly(rac-2), (in *CDCl$_3$, 150 MHz)

Figure S 42. $^1$H-$^1$H COSY spectrum of Poly(rac-2), (in CDCl$_3$, 500 MHz)
Figure S 43. $^1$H-NMR spectrum of Poly(rac-2) (CDCl$_3$, 400 MHz). Deconvolution of the peaks were used to determine the %HT and % trans of the polymer.

\[
\text{% HT} = \frac{\text{area of cis - HT + trans - HT}}{\text{total area cis - HT + trans - HH + trans - HT}} \times 100 = 68.3 \%.
\]

\[
\text{% trans} = \frac{\text{area of trans - HH + trans - HT}}{\text{total area cis - HT + trans - HH + trans - HT}} \times 100 = 94.2 \%.
\]
**Figure S 44.** SEC RI trace of Poly(rac-2). ($\bar{D} = 2.07$, $\text{Mn} = 41.6$ kDa)
Figure S 45. $^1$H NMR spectrum of Poly(rac-1), (*DMF-$d_7$, 600 MHz)
**Figure S 46.** $^{13}$C NMR spectrum of Poly(rac-1), (*DMF$_7$, 150 MHz)
Figure S 47. $^1$H-$^1$H COSY spectra of Poly(rac-1) (CDCl$_3$, 600 MHz)
Figure S 48. $^1$H-NMR spectrum of Poly(rac-1) (CDCl$_3$, 400 MHz). Deconvolution of the peaks were used to determine the %HT and % trans of the polymer.

$$\% HT = \frac{\text{area of cis} - \text{HT} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 57 \%.$$

$$\% \text{trans} = \frac{\text{area of trans} - \text{HH} + \text{trans} - \text{HT}}{\text{total area cis} - \text{HT} + \text{trans} - \text{HH} + \text{trans} - \text{HT}} \times 100 = 91 \%.$$
Table S49: Aliquot characterization of Poly(rac-3) at 2.5 M with HG2 at -10 °C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conv(^a) %</th>
</tr>
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<tbody>
<tr>
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<tr>
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<td>33.3</td>
</tr>
<tr>
<td>157</td>
<td>33.3</td>
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</table>

\(^a\) Determined by \(^1\)H NMR (400 MHz in CDCl\(_3\)).
Figure S50. Equilibrium conversion of Poly(rac-3) with respect to time.
Figure S51. TGA analysis of poly(rac-1), poly(rac-2) and poly(rac-3) after equilibration at 110 °C followed by heating at 10 °C min⁻¹ to 750 °C under argon.
Figure S52. Differential scanning calorimetry thermograms of each polymer sample. The thermal range chosen was based on the minimum temperature for the instrument (-70 °C) and the temperature at which thermal decomposition of the polymer is suspected (~200 °C) based on TGA. Jagged baseline noise is present above 100 °C on some samples and was determined to be an artifact of the instrument by repeated cycles where this noise was found inconsistent.

References: