Supporting information

The influence of branching on the Kumada catalyst transfer condensative polymerization of 3-alkylthiophenes

Lize Verheyen\textsuperscript{a}, Birgitt Timmermans\textsuperscript{a} and Guy Koeckelberghs\textsuperscript{*a}

\textsuperscript{a}Laboratory for Polymer Synthesis, KU Leuven, Celestijnenlaan 200F - Box 2404, B-3001 Heverlee, Belgium

Contents
I. Materials ........................................................................................................................................... 2
II. Instrumentation ............................................................................................................................... 2
III. Synthetic procedures ..................................................................................................................... 2
  a. Synthesis of precursor monomer ............................................................................................... 2
  b. Monomer synthesis ..................................................................................................................... 5
IV. Polymerization procedures .......................................................................................................... 5
  a. Synthesis of P3ODT (P3ODT-1) ............................................................................................... 5
  b. Chain extension experiment of P3ODT (P3ODT-2a and P3ODT-2b) ..................................... 6
  c. General procedure for kinetic experiments ............................................................................. 6
  d. General procedure for variation of the degree of polymerization (P3ODT-3a-e and P3HT-3a-e) 6
  e. General procedure for multiple chain extension (P3ODT-4a-i and P3HT-4a-i) .................... 7
  f. General procedure for chain extension after different periods of time (P3ODT-5a-c, P3ODT-6a-c, P3HT-5a,c,d and P3HT-6a,c,d) ........................................................................ 8
  g. Polymer end group characterization with \textsuperscript{1}H NMR (P3ODT-7 and P3HT-7) ............... 8
V. NMR spectra ..................................................................................................................................... 9
VI. Additional GPC elution curves ...................................................................................................... 13
VII. Kinetic rate studies ...................................................................................................................... 14
I. Materials
All reagents were purchased and used without further purification. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina).

II. Instrumentation
$^1$H-NMR spectra were recorded on a Bruker Avance 300 MHz and Bruker Avance 600 MHz spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a Shimadzu 10A GPC system. The column is a PLgel 5μm mixed-D type column and the detection system consists of a differential refractometer and a UV-vis spectrophotometer. The GPC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF ($c \approx 1$ mg/mL) and filtered over a pore size of 0.2 μm. The GC-MS spectra were recorded using a Thermo Finnigan Trace GC and ITQ 9000 Mass Spectrometer.

III. Synthetic procedures

a. Synthesis of precursor monomer

*Synthesis of 9-(bromomethyl)nonadecane (I)*

$N$-bromosuccinimide (11.1 g, 62.5 mmol) was slowly added to a flask charged with 2-octyldodecan-1-ol (14.9 g, 50.0 mmol), PPh$_3$ (16.4 g, 62.5 mmol) and DCM (160 mL) under argon at 0°C. The reaction mixture was protected from light and stirred at room temperature overnight. Heptane was added and the formed precipitate was filtered off, re-dissolved in DCM, again precipitated in heptane and filtered. The combined organic layers were consecutively washed with a Na$_2$S$_2$O$_3$-, NaOH-, NaHCO$_3$- and NaCl-solution, dried over
MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography with heptane and a colourless product was obtained.

Yield: 16.50 g, 91%. δH (300 MHz; CDCl₃; TMS) 3.45 (d, 2H), 1.27 (m, 33 H), 0.88 (t, 6H). δC (300 MHz; CDCl₃; TMS) 39.7, 39.5, 32.6, 31.92, 31.90, 29.8, 29.64, 29.60, 29.56, 29.4, 29.3, 26.6, 22.7, 14.1. MS (EI) m/z: 281.8 [M⁺-Br], 247.6 [M⁺-C₈H₁₇], 141.4 [M⁺-C₁₀H₂₁Br], 113.3 [M⁺-C₁₂H₂₅Br].

**Synthesis of 3-(2-octyldecyl)thiophene (2)**

A solution of 9-(bromomethyl)nonadecane (1) (17.4 g, 48.1 mmol) in dry diethyl ether (30 mL) was added dropwise to a suspension of magnesium turnings (1.17 g, 48.1 mmol) in dry diethyl ether (10 mL) under inert atmosphere and the reaction mixture was refluxed during 2 hours. When the reaction mixture reached room temperature again, it was added dropwise to a solution of 3-bromothiophene (7.68 g, 47.1 mmol) and Ni(dppp)Cl₂ (0.261 g, 0.481 mmol) in dry diethyl ether (10 mL) under inert atmosphere. The reaction mixture was refluxed during 2 hours, after which it was poured into a 2 M HCl solution at 0°C. The formed precipitate was filtered off and the filtrate was extracted with diethyl ether. The combined organic layers were consecutively washed with a NaHCO₃- and a NaCl-solution, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography with heptane and a colourless product was obtained.

Yield: 4.94 g, 28%. δH (300 MHz; CDCl₃; TMS) 7.22 (d, 1H, J = 2.93, 4.90 Hz), 6.89 (m, 2H), 2.55 (d, 2H), 1.61 (m, 1H), 1.25 (m, 32H), 0.88 (dt, 6H). δC (300 MHz; CDCl₃; TMS) 141.9, 128.8, 124.8, 120.6, 38.9, 34.7, 33.3, 31.9, 30.0, 29.69, 29.67, 29.65, 29.38, 29.36, 22.7, 14.1. MS (EI) m/z: 365.1 [M⁺], 251.8 [M⁺-C₈H₁₇], 223.2 [M⁺-C₁₀H₂₁], 111.4 [M⁺-C₁₆H₁₇S], 97.5 [M⁺-C₁₉H₉₉].
Synthesis of 2-bromo-3-(2-octyldodecyl)thiophene (3)

N-bromosuccinimide (2.20 g, 12.4 mmol) was slowly added to a flask charged with 3-(2-octyldodecyl)thiophene (2) (4.90 g, 13.4 mmol) in THF (55 mL) at 0°C under inert atmosphere. The reaction mixture was shielded from light and stirred at room temperature overnight. Then, water (55 mL) was added and the whole mixture was extracted with heptane. The combined organic layers were consecutively washed with a Na₂S₂O₅-, NaOH-, NaHCO₃- and NaCl-solution, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified using column chromatography with petroleum ether and a colourless product was obtained.

Yield: 4.50 g, 76%.  δH (300 MHz; CDCl₃; TMS) 7.17 (d, 1H, J = 5.6 Hz), 6.75 (d, 1H, J = 5.6 Hz), 2.48 (d, 2H), 1.64 (m, 1H), 1.25 (m, 32H), 0.88 (t, 6H). δC (300 MHz; CDCl₃; TMS) 141.2, 128.8, 124.9, 109.4, 38.5, 34.0, 33.3, 31.94, 33.93, 33.0, 29.7, 29.6, 29.37, 29.35, 29.5, 22.7, 14.1, 0.0. MS (EI) m/z: 443.0 [M⁺], 364.1 [M⁺-Br], 175.5 [M⁺-C₁₉H₃₉], 139.6 [M⁺-C₁₄H₂₂BrS], 111.5 [M⁺-C₁₆H₁₇BrS], 97.4 [M⁺-C₁₉H₃₀Br].

Synthesis of 2-bromo-5-iodo-3-(2-octyldodecyl)thiophene (4)

Iodine (1.29 g, 5.07 mmol) and diacetoxyiodo)benzene (1.63 g, 5.07 mmol) were added to a flask charged with 2-bromo-3-(2-octyldodecyl)thiophene (3) (4.90 g, 10.1 mmol) in DCM (80 mL) at 0°C under inert atmosphere. The reaction mixture was stirred at room temperature overnight, after which it was extracted with diethyl ether. The combined organic layers were consecutively washed with a NaHCO₃- and a NaCl-solution, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified using vacuum distillation and column chromatography with petroleum ether. A colourless product was obtained.
Yield: 5.42 g, 94%. δH (300 MHz; CDCl₃; TMS) 6.92 (s, 1H), 2.44 (d, 2H), 1.61 (m, 1H), 1.25 (m, 32H), 0.88 (t, 6H) . δC (300 MHz; CDCl₃; TMS) 143.5, 138.4, 112.3, 71.0, 38.6, 33.8, 33.2, 31.97, 31.95, 30.0, 29.69, 29.67, 29.62, 29.40, 29.36, 26.5, 22.7, 14.2. MS (EI) m/z: 569.2 [M⁺], 490.2 [M⁺-Br], 444.2 [M⁺-I], 363.1 [M⁺-BrI], 223.6 [M⁺-C₁₉H₃₉Br], 97.4 [M⁺-C₁₉H₃₉BrI].

b. Monomer synthesis

*Synthesis of monomer 5*

Precursor monomer 4 (285 mg, 0.5 mmol) was brought under argon atmosphere and dissolved in dry THF (5mL). An iPrMgCl•LiCl-solution (475 μmol, 380 μL, 1.25 M) was added dropwise and was stirred for 30 minutes to complete the Grignard Metathesis.

*Synthesis of monomer 6*

2-bromo-5-iodo-3-(hexyl)thiophene (187 mg, 0.5 mmol) was brought under argon atmosphere and dissolved in dry THF (5mL). An iPrMgCl•LiCl-solution (475 μmol, 380 μL, 1.25 M) was added dropwise and was stirred for 30 minutes to complete the Grignard Metathesis.

**IV. Polymerization procedures**

a. Synthesis of P3ODT (P3ODT-1)

3 mL of a 0.1 M solution of monomer 5 in THF was cannulated to a flask containing Ni(dpdp)Cl₂ (1.62 mg, 3.00 μmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1 hour the polymerization is terminated by the addition of acidified THF. The whole mixture is stirred for 1 hour before the crude polymerization mixture was analysed with GPC.

\[M_n = 22 \text{ kg/mol}; D = 1.05\]
b. Chain extension experiment of P3ODT (P3ODT-2a and P3ODT-2b)

3 mL of a 0.1 M solution of monomer 5 in THF was cannulated to a flask containing Ni(dppp)Cl₂ (1.62 mg, 3.00 μmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1 hour a quench of the polymerization is taken and new monomer 5 (1.5 mL, 0.1 M) is added. After 1 hour the polymerization is terminated by the addition of acidified THF. The whole mixture is stirred for 1 hour before the crude polymerization mixture was analysed with GPC.

P3ODT-2a: $\bar{M}_n = 22$ kg/mol; $D = 1.05$

P3ODT-2b: $\bar{M}_n = 38$ kg/mol; $D = 1.1$

c. General procedure for kinetic experiments

1 mL of a 0.1 M solution of monomer 5 or 6 in THF was cannulated to a flask containing Ni(dppp)Cl₂ (5.4 mg, 10 μmol) in THF (0.5 mL) under argon atmosphere to start the polymerization. After 10 minutes a second batch of monomer 5 or 6 (4 mL, 0.1 M), containing a polystyrene standard (40 mg, $\bar{M}_p = 174$ kg/mol) was added and from that point a sample was taken every 30 seconds. The samples were terminated with acidified THF and analysed with GPC.

d. General procedure for variation of the degree of polymerization (P3ODT-3a-e and P3HT-3a-e)

15 mL of a 0.1 M solution of monomer 5 or 6 in THF was prepared and divided over 5 flasks containing respectively 20 μmol (10.8 mg), 6.0 μmol (3.25 mg), 3.0 μmol (1.63 mg), 2.0 μmol (1.08 mg) and 1.5 μmol (813 μg) Ni(dppp)Cl₂ in THF (0.5 mL). After 1 hour the polymerization was terminated with acidified THF. The whole mixture is stirred for 1 hour before the crude reaction mixtures were analysed with GPC.
<table>
<thead>
<tr>
<th></th>
<th>P3ODT</th>
<th></th>
<th>P3HT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{M}_n$ (kg/mol)</td>
<td>$\mathcal{D}$</td>
<td>$\bar{M}_n$ (kg/mol)</td>
<td>$\mathcal{D}$</td>
</tr>
<tr>
<td>3a ([M]/[In]=15)</td>
<td>6.6</td>
<td>1.07</td>
<td>2.9</td>
<td>1.3</td>
</tr>
<tr>
<td>3b ([M]/[In]=50)</td>
<td>16</td>
<td>1.05</td>
<td>11</td>
<td>1.1</td>
</tr>
<tr>
<td>3c ([M]/[In]=100)</td>
<td>26</td>
<td>1.07</td>
<td>21</td>
<td>1.1</td>
</tr>
<tr>
<td>3d ([M]/[In]=150)</td>
<td>37</td>
<td>1.12</td>
<td>35</td>
<td>1.2</td>
</tr>
<tr>
<td>3e ([M]/[In]=200)</td>
<td>38</td>
<td>1.11</td>
<td>40</td>
<td>1.2</td>
</tr>
</tbody>
</table>

e. General procedure for multiple chain extension (P3ODT-4a-i and P3HT-4a-i)

2 mL of a 0.2 M solution of monomer 5 or 6 in THF was cannulated to a flask containing Ni(dppp)Cl$_2$ (5.4 mg, 10 µmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1, 2, 3, 4, 5, 6, 7 and 8 hours after the start of the polymerization another batch of monomer (10 equivalents) was added to the polymerization mixtures. Before the addition of each block, a sample was taken, which was terminated with acidified THF and analysed with GPC.
f. General procedure for chain extension after different periods of time (P3ODT-5a-c, P3ODT-6a-c, P3HT-5a-c,d and P3HT-6a,c,d)

1.4 mmol (0.2 M or 0.05 M in THF) of monomer 5 or 6 in THF was cannulated to a flask containing Ni(dppp)Cl₂ (37.9 mg, 70 μmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1 hour the polymerization mixture is divided over 7 flasks and stored in a desiccator. After different periods of time a fresh monomer solution of 5 or 6 (0.20 mmol, 0.2 M or 0.05 M) was added to the different flasks. After 1 hour the polymerization was terminated with acidified THF. The whole mixture is stirred for 1 hour before the crude reaction mixtures were analysed with GPC.

g. Polymer end group characterization with \(^1\)H NMR (P3ODT-7 and P3HT-7)

5 mL of a 0.1 M solution of monomer 5 or 6 in THF was cannulated to a flask containing Ni(dppp)Cl₂ (13.6 mg, 25 μmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1 week the polymerization is terminated by the addition of acidified
THF. The whole mixture is stirred for 1 hour before the polymer is precipitated in methanol. The polymer is then purified using a Soxhlet extraction with methanol and chloroform. The chloroform-soluble fraction was again precipitated in methanol, filtered and dried under vacuum.

**P3ODT-7**: $\overline{M}_n = 6$ kg/mol; $D = 1.1$

**P3HT-7**: $\overline{M}_n = 4$ kg/mol; $D = 1.2$

V. NMR spectra

1H NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)

$^1$H NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)

$^{13}$C NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)
$^{13}$C NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)

$^1$H NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)
Assignment of the aromatic signals for P3HT-7 was done according to literature\(^1\). Based on the aromatic signals, the percentage of decomplexation equals 38 %, which is in good agreement with the result obtained from the aliphatic region (39 %)

\[
\% \text{(decomplexation)} = \left( \frac{0.9538 - 0.4329}{0.9538 + 0.4329} \right) \times 100 \% = 38 \%
\]
VI. Additional GPC elution curves

GPC elution curves of P3HT and P3ODT after 1 hour of polymerization (P3HT-7a and P3ODT-7a) and after one week (P3HT-7b and P3ODT-7b).
VII. Kinetic rate studies

1) Determination of propagation rate constant for P3HT

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>([M]/[PS])/(([M]/[PS])₀)</th>
<th>Ln([M]/[PS])/(([M]/[PS])₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.004</td>
<td>0.003497</td>
</tr>
<tr>
<td>1</td>
<td>0.9559</td>
<td>-0.04511</td>
</tr>
<tr>
<td>1.5</td>
<td>0.8866</td>
<td>-0.1204</td>
</tr>
<tr>
<td>2</td>
<td>0.8396</td>
<td>-0.1749</td>
</tr>
<tr>
<td>2.5</td>
<td>0.7882</td>
<td>-0.2381</td>
</tr>
<tr>
<td>3</td>
<td>0.7975</td>
<td>-0.2263</td>
</tr>
<tr>
<td>3.5</td>
<td>0.7599</td>
<td>-0.2745</td>
</tr>
<tr>
<td>4</td>
<td>0.7531</td>
<td>-0.2836</td>
</tr>
<tr>
<td>4.5</td>
<td>0.7486</td>
<td>-0.2896</td>
</tr>
<tr>
<td>6</td>
<td>0.6513</td>
<td>-0.4288</td>
</tr>
</tbody>
</table>

The linear regression of the data points resulted in the following equation: y = (-0.073 ± 0.006) x + (0 ± 0.02) (R² = 0.9421) in which the slope is equal to −k·[In] (equation S1). Therefore the rate constant equals 40 ± 4 L mol⁻¹ s⁻¹.
\[
\ln \frac{([M]/[PS])_t}{([M]/[PS])_0} = -k [In] t
\]

Eq. S1

2) Determination of propagation rate constant for P3OD

| Time (min) | \(([M]/[PS])_t/([M]/[PS])_0\) | \(
\ln([M]/[PS])_t/([M]/[PS])_0\) |
<table>
<thead>
<tr>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.9555</td>
<td>-0.04551</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9087</td>
<td>-0.09579</td>
</tr>
<tr>
<td>3.5</td>
<td>0.8350</td>
<td>-0.1803</td>
</tr>
<tr>
<td>4.5</td>
<td>0.8368</td>
<td>-0.1782</td>
</tr>
<tr>
<td>5.5</td>
<td>0.7785</td>
<td>-0.2504</td>
</tr>
<tr>
<td>6.5</td>
<td>0.7844</td>
<td>-0.2428</td>
</tr>
</tbody>
</table>

The linear regression of the data points resulted in the following equation: \(y = (-0.041 \pm 0.006) x + (0 \pm 0.03)\) \((R^2 = 0.9129)\) in which the slope is equal to \(-k\cdot[In]\) (equation S1).

Therefore the rate constant equals \(23 \pm 4 \text{ L mol}^{-1} \text{ s}^{-1}\). 