Supporting information

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

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Contents

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 ≈ 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 (**1**)*

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 $Na_2S_2O_5$-, NaOH-, $NaHCO_3$- and NaCl-solution, dried over

$MgSO_4$ 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; $CDCl_3$; TMS) 3.45 (d, 2H), 1.27 (m, 33 H), 0.88 (t, 6H). δC (300 MHz; $CDCl_3$; 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^+-C_8H_{17}], 141.4 [M^+-$C_{10}H_{20}Br$], 113.3 [M^+-$C_{12}H_{24}Br$].

*Synthesis of 3-(2-octyldodecyl)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)Cl_2 (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 $NaHCO_3$- and a NaCl-solution, dried over $MgSO_4$ 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; $CDCl_3$; 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; $CDCl_3$; 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^+-C_8H_{17}], 223.2 [M^+-$C_{10}H_{21}$], 111.4 [M^+-$C_{16}H_{17}S$], 97.5 [M^+-$C_{19}H_{39}$].

*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 $Na_2S_2O_5$-, NaOH-, $NaHCO_3$- and NaCl-solution, dried over $MgSO_4$ 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; $CDCl_3$; 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; $CDCl_3$; 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^+-$C_{19}H_{39}$], 139.6 [M^+-$C_{14}H_{22}BrS$], 111.5 [M^+-$C_{16}H_{17}BrS$], 97.4 [M^+-$C_{19}H_{39}Br$].

*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 $NaHCO_3$- and a NaCl-solution, dried over $MgSO_4$ 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; $CDCl_3$; TMS) 6.92 (s, 1H), 2.44 (d, 2H), 1.61 (m, 1H), 1.25 (m, 32H), 0.88 (t, 6H) . δC (300 MHz; $CDCl_3$; 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^+-$C_{19}H_{39}Br$], 97.4 [M^+-$C_{19}H_{39}BrI$].

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 *i*PrMgCl•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 *i*PrMgCl•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(dppp)Cl_2 (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.

$\overline{M}_n$ = 22 kg/mol; Đ = 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)Cl_2 (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: $\overline{\mathrm{M}}_\mathrm{n}$= 22 kg/mol; Đ = 1.05

P3ODT-2b: $\overline{\mathrm{M}}_\mathrm{n}$ = 38 kg/mol; Đ = 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)Cl_2 (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, $\overline{\mathrm{M}}_\mathrm{p} = 174\ \mathrm{kg/mol}$) 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)Cl_2 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.

	P3ODT		P3HT	
	$\overline{M}_n$(kg/mol)	Đ	$\overline{M}_n$ (kg/mol)	Đ
3a ($[M]_0/[In]=15$)	6.6	1.07	2.9	1.3
3b ($[M]_0/[In]=50$)	16	1.05	11	1.1
3c ($[M]_0/[In]=100$)	26	1.07	21	1.1
3d ($[M]_0/[In]=150$)	37	1.12	35	1.2
3e ($[M]_0/[In]=200$)	38	1.11	40	1.2

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.

	P3ODT		P3HT	
	$\overline{M}_n$(kg/mol)	Đ	$\overline{M}_n$ (kg/mol)	Đ
4a ($[M]_0/[In]=20$)	6.4	1.08	3.3	1.3
4b ($[M]_0/[In]=30$)	8.1	1.07	5.7	1.2
4c ($[M]_0/[In]=40$)	12	1.06	7.4	1.1
4d ($[M]_0/[In]=50$)	14	1.05	8.7	1.1
4e ($[M]_0/[In]=60$)	16	1.06	10	1.1
4f ($[M]_0/[In]=70$)	18	1.06	12	1.1
4g ($[M]_0/[In]=80$)	19	1.11	13	1.1
4h ($[M]_0/[In]=90$)	21	1.12	15	1.2
4i ($[M]_0/[In]=100$)	21	1.14	17	1.1

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)Cl_2 (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**)

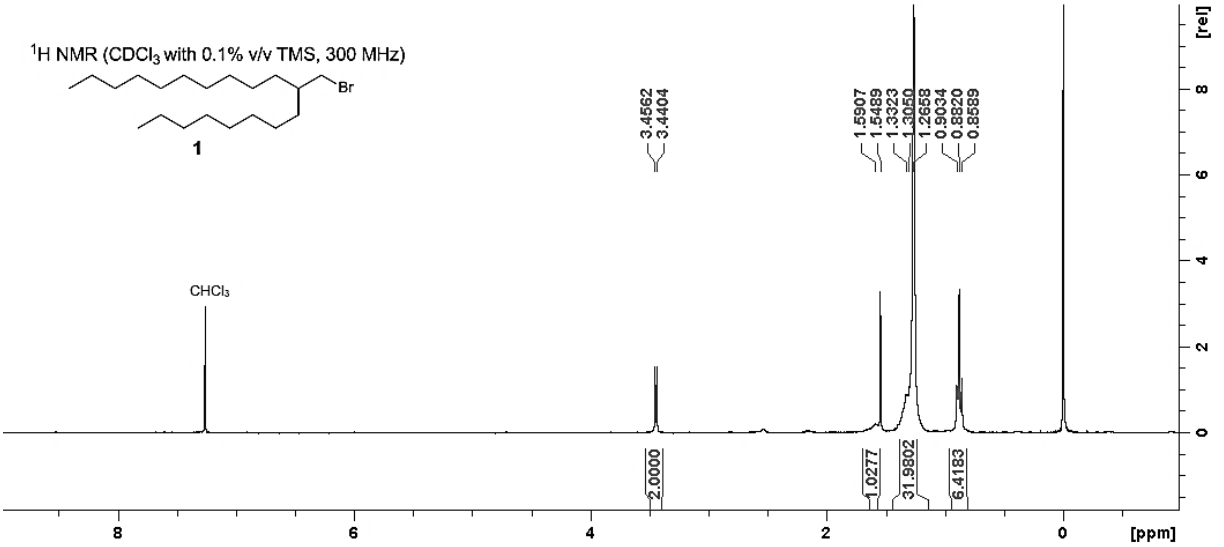
5 mL of a 0.1 M solution of monomer **5** or **6** in THF was cannulated to a flask containing Ni(dppp)Cl_2 (13.6 mg, 25 µmol) in THF (1 mL) under argon atmosphere to start the polymerization. After 1 week the polymerization is terminated by the addition of acidified

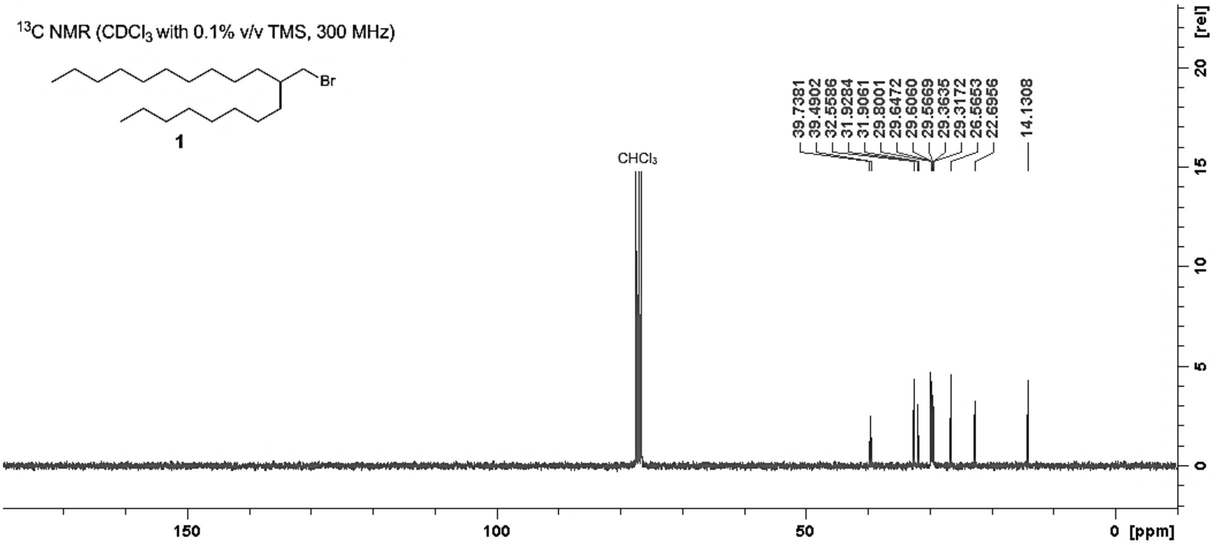
THF. The whole mixture is stirred for 1 hour before the polymer is precipitated in methanol. The polymer is then purified using a Soxhlet extraction with methanol and chloroform. The chloroform-soluble fraction was again precipitated in methanol, filtered and dried under vacuum.

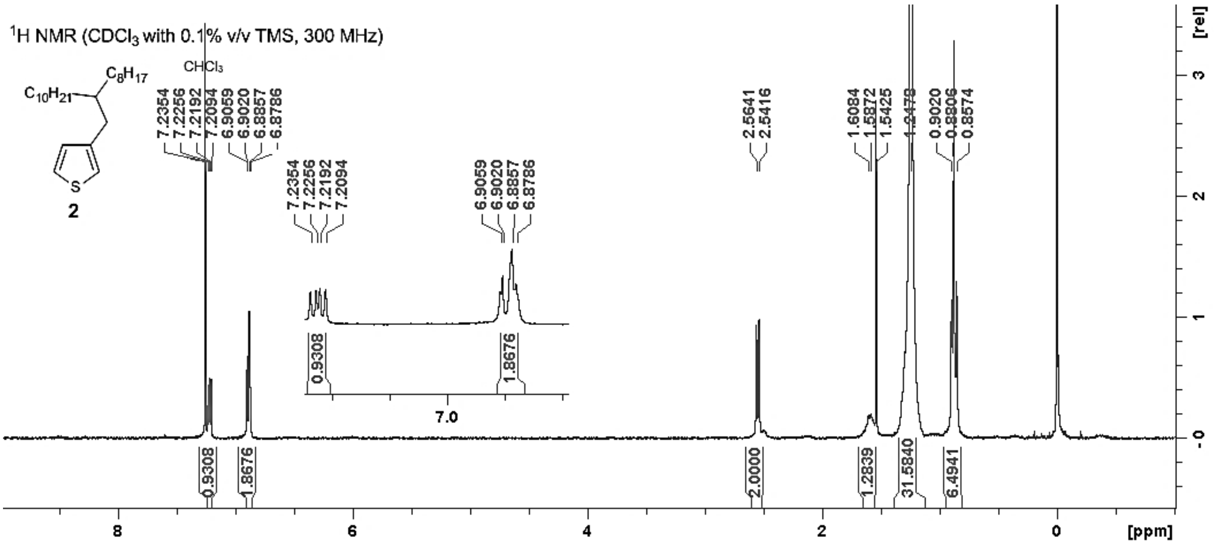
P3ODT-7: $\overline{M}_n$= 6 kg/mol; Đ = 1.1

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

V. NMR spectra






1H NMR (CDCl3 with 0.1% v/v TMS, 300 MHz)
CHCl3
C10H21
C8H17
S
2
7.2354
7.2256
7.2192
7.2094
6.9059
6.9020
6.8857
6.8786
2.5641
2.5416
1.6084
1.5872
1.5425
1.2478
0.9020
0.8806
0.8574
0.9308
1.8676
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2.0000
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1
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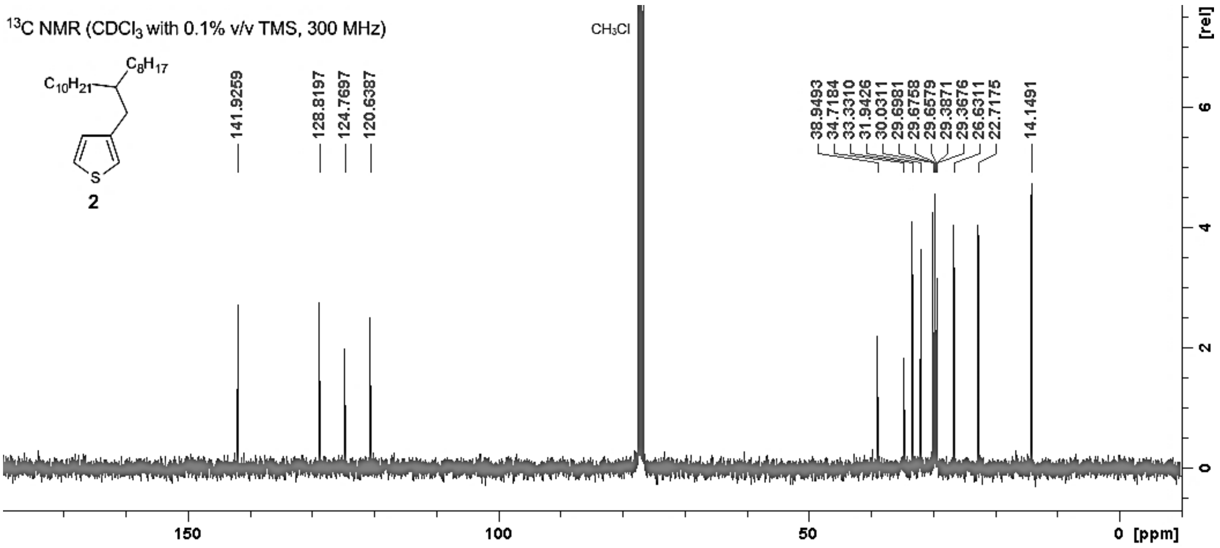
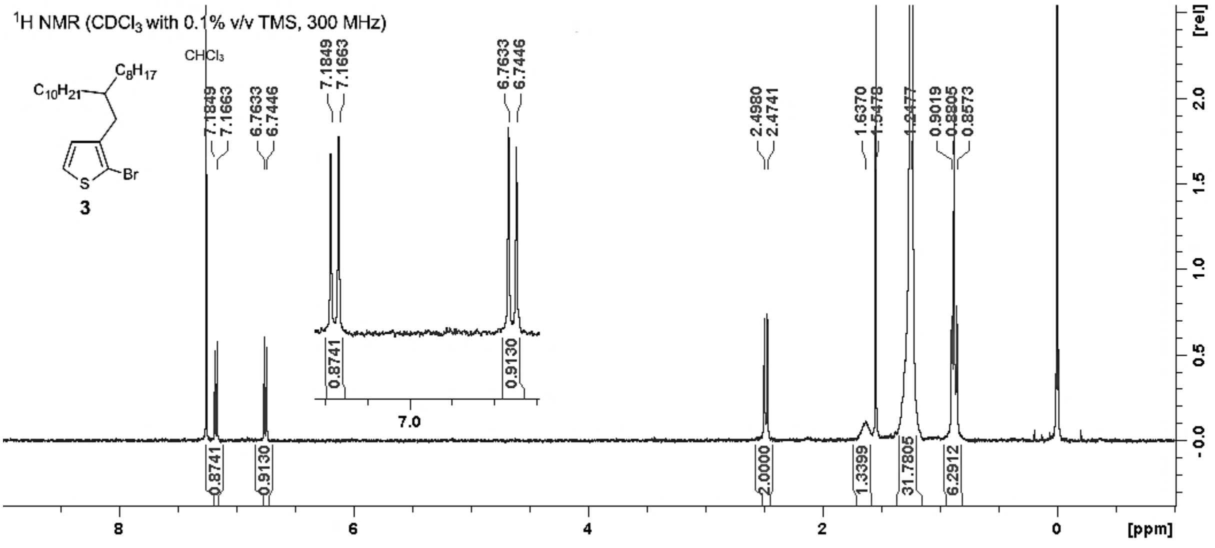

13C NMR (CDCl3 with 0.1% v/v TMS, 300 MHz)
C10H21
C8H17
S
2
CH3Cl
141.9259
128.8197
124.7697
120.6387
38.9493
34.7184
33.3310
31.9426
30.0311
29.6981
29.6758
29.6579
29.3871
29.3676
26.6311
22.7175
14.1491
150
100
50
0
[ppm]
[rel]
6
4
2
0


1H NMR (CDCl3 with 0.1% v/v TMS, 300 MHz)
CHCl3
C10H21
C8H17
S
Br
3
7.1849
7.1663
6.7633
6.7446
2.4980
2.4741
1.6370
1.5478
1.2477
0.9019
0.8805
0.8573
0.8741
0.9130
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2.0000
1.3399
31.7805
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0.5
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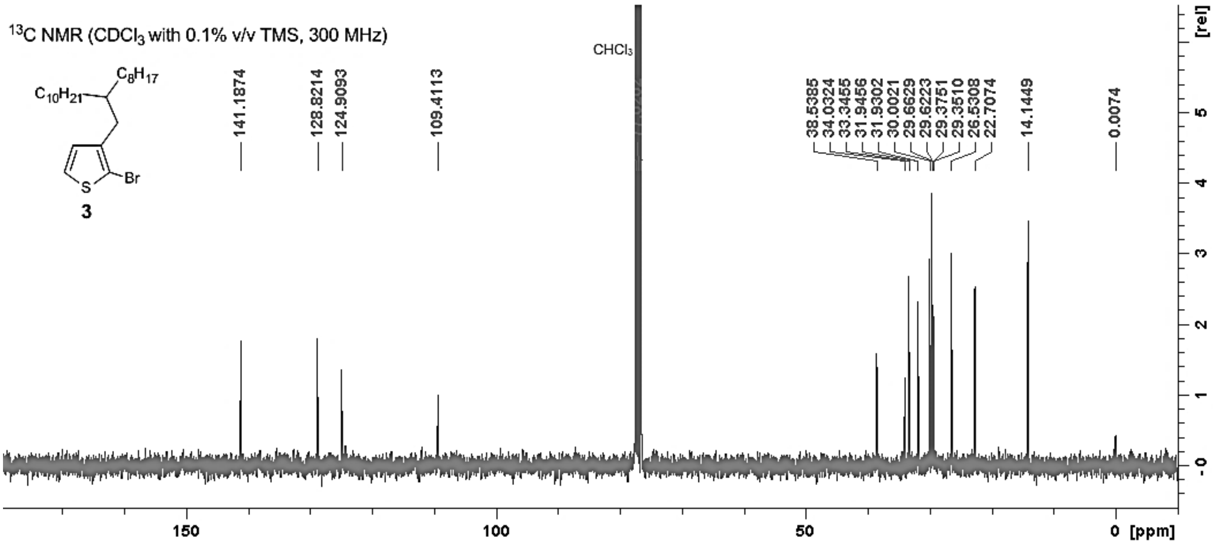
^{13}C NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)
$C_{10}H_{21}$
C_8H_{17}
S
Br
3
CHCl$_3$
141.1874
128.8214
124.9093
109.4113
38.5385
34.0324
33.3455
31.9456
31.9302
30.0021
29.6629
29.6223
29.3751
29.3510
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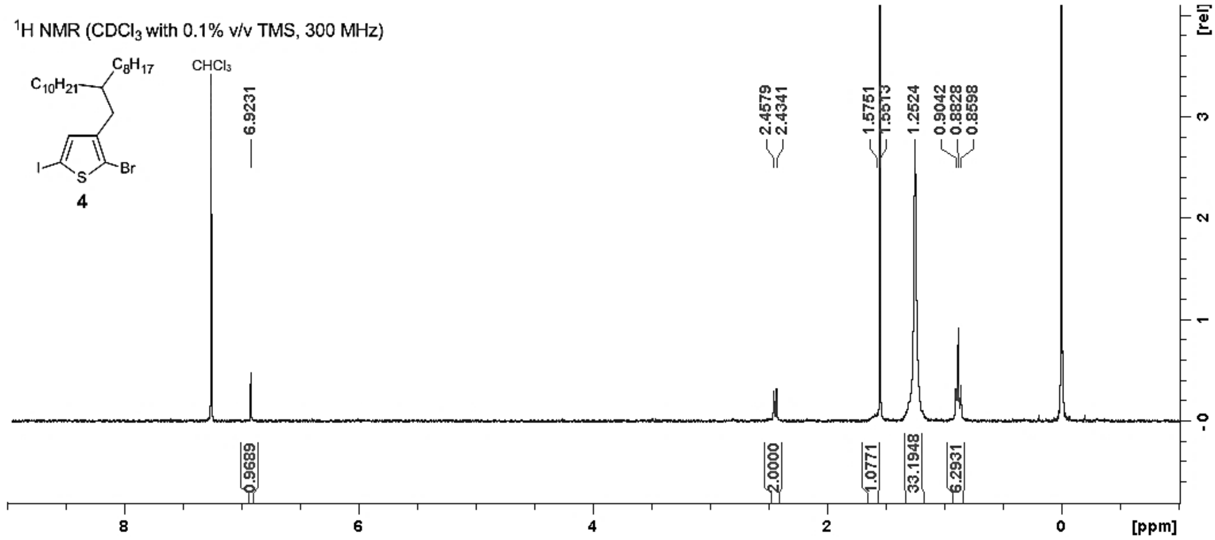
^{1}H NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)
$C_{10}H_{21}$
C_8H_{17}
I
S
Br
4
CHCl$_3$
6.9231
2.4579
2.4341
1.5751
1.5513
1.2524
0.9042
0.8828
0.8598
0.9689
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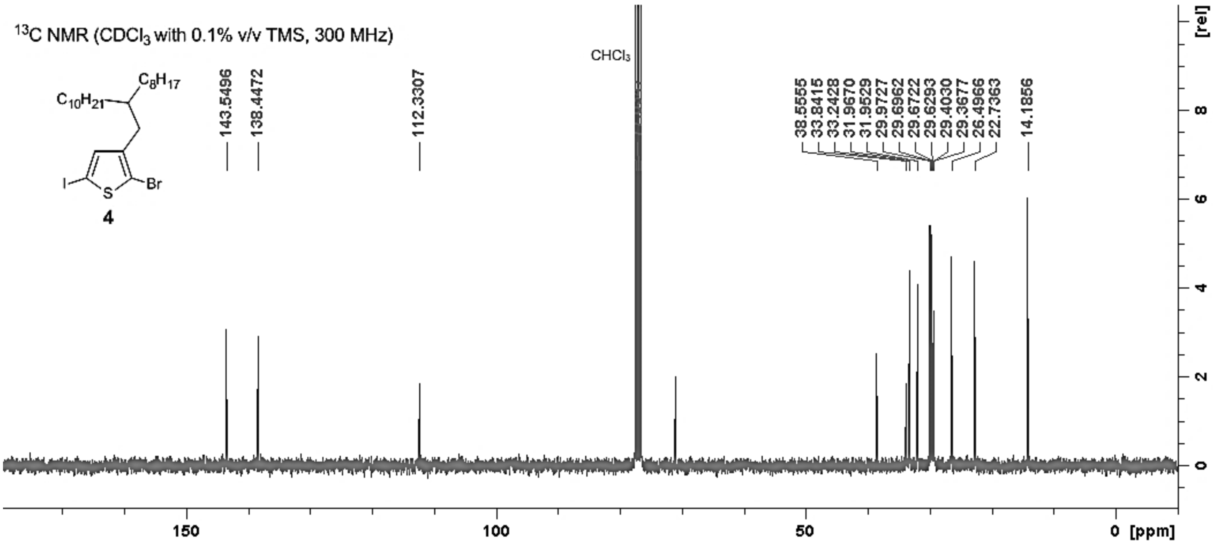
^{13}C NMR (CDCl$_3$ with 0.1% v/v TMS, 300 MHz)
$C_{10}H_{21}$
C_8H_{17}
I
S
Br
4
CHCl$_3$
143.5496
138.4472
112.3307
38.5555
33.8415
33.2428
31.9670
31.9529
29.9727
29.6962
29.6722
29.6293
29.4030
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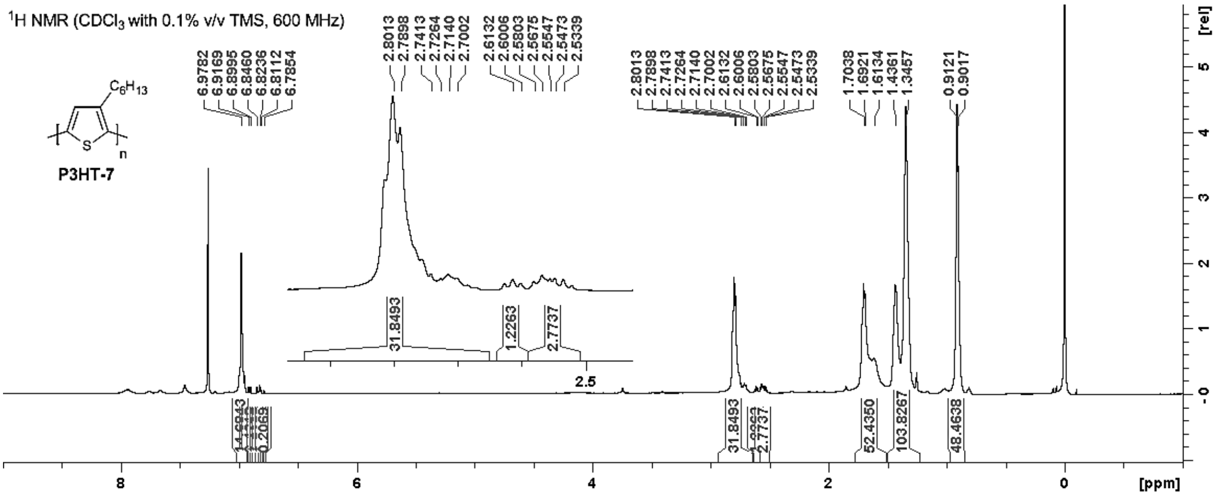
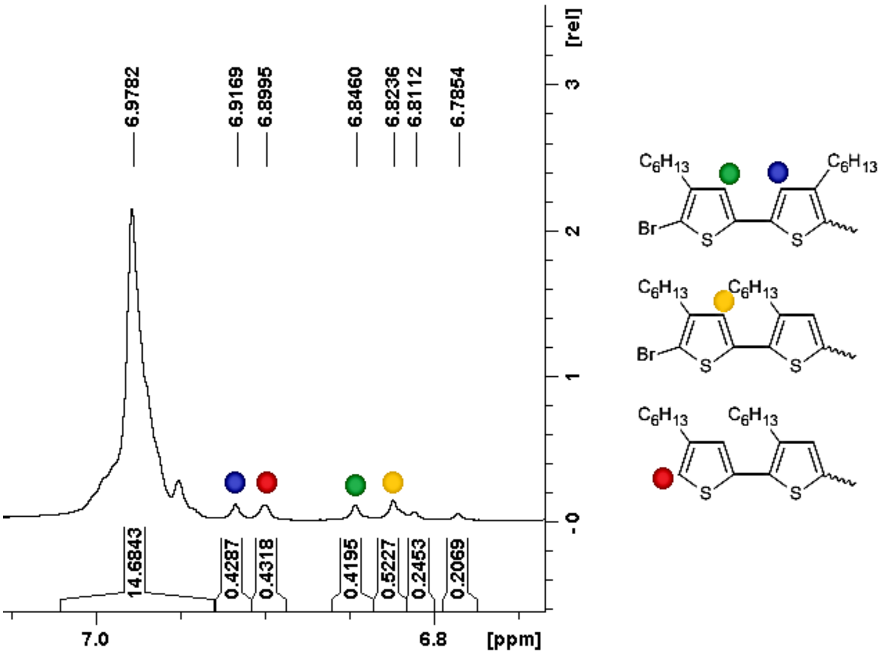
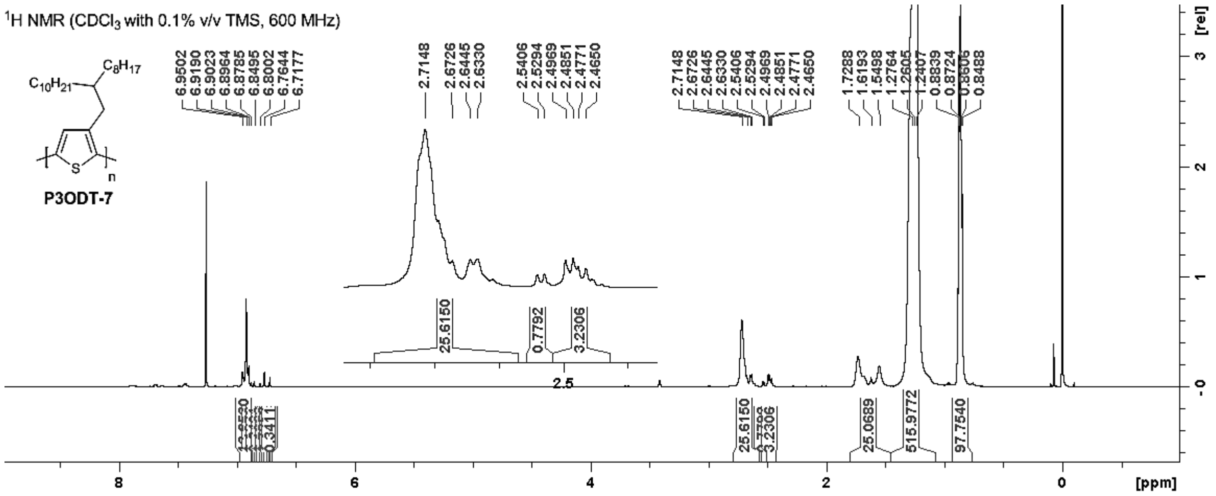
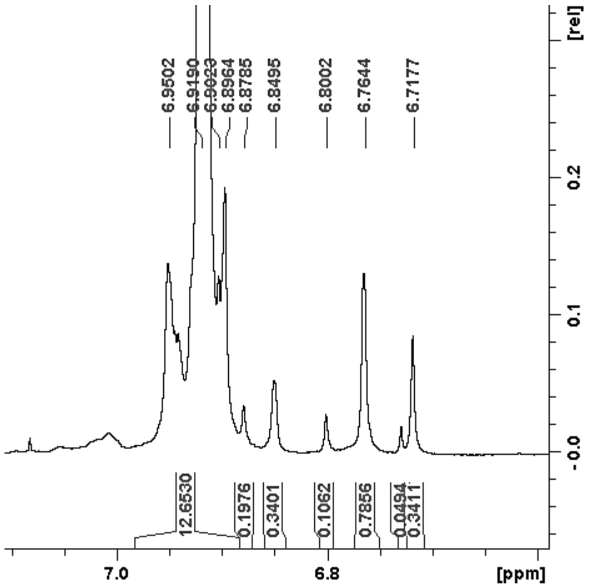




Assignment of the aromatic signals for **P3HT-7** was done according to literature[1]. Based on the aromatic signals, the percentage of decomplexation equals 38 %, which is in good agreement with the result obtained from the aliphatic region (39 %)

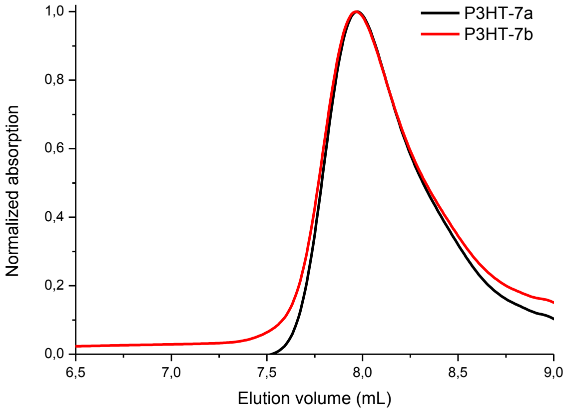
$$\%(\text{decomplexation}) = \frac{\left(\frac{0.9538 - 0.4329}{2}\right)}{\left(\frac{0.9538 + 0.4329}{2}\right)} . 100\ \% = 38\ \%$$

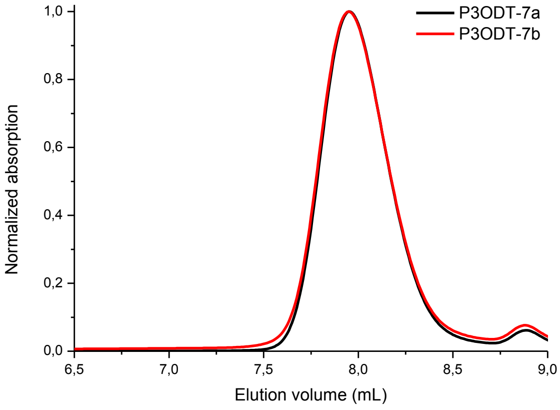




VI. Additional GPC elution curves

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

Time (min)	$([M]/[PS])_t/([M]/[PS])_0$	$\mathrm{Ln}(([M]/[PS])_t/([M]/[PS])_0)$
0,5	1.004	0.003497
1	0.9559	-0.04511
1,5	0.8866	-0.1204
2	0.8396	-0.1749
2,5	0.7882	-0.2381
3	0.7975	-0.2263
3,5	0.7599	-0.2745
4	0.7531	-0.2836
4,5	0.7486	-0.2896
6	0.6513	-0.4288

The linear regression of the data points resulted in the following equation: $y = (-0.073 \pm 0.006)\,x + (0 \pm 0.02)$ ($R^2 = 0.9421$) in which the slope is equal to $-k \cdot [In]$ (equation S1). Therefore the rate constant equals 40 ± 4 L mol^{-1} s^{-1}.

$$\ln\frac{([\mathrm{M}]/[\mathrm{PS}])_t}{([\mathrm{M}]/[\mathrm{PS}])_0} = -k[In]t \qquad \text{Eq. S1}$$

2) Determination of propagation rate constant for P3OD

Time (min)	$([M]/[PS])_t/([M]/[PS])_0$	$\mathrm{Ln}([M]/[PS])_t/([M]/[PS])_0)$
1,5	0.9555	-0.04551
2,5	0.9087	-0.09579
3,5	0.8350	-0.1803
4,5	0.8368	-0.1782
5,5	0.7785	-0.2504
6,5	0.7844	-0.2428

The linear regression of the data points resulted in the following equation: y = (-0.041 ± 0.006) x + (0 ± 0.03) ($R^2 = 0.9129$) in which the slope is equal to $-k\cdot[In]$ (equation S1). Therefore the rate constant equals 23 ± 4 L mol^{-1} s^{-1}.

1 P. Kohn, S. Huettner, H. Komber, V. Senkovskyy, R. Tkachov, A. Kiriy, R. H. Friend, U. Steiner, W. T. S. Huck, J. U. Sommer and M. Sommer, *J. Am. Chem. Soc.*, 2012, **134**, 4790–4805.