SUPPORTING INFORMATION

The influence of the end-group on the self-assembly of

conjugated block copolymers

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EXPERIMENTAL INFORMATION

All reagents were purchased from Sigma Aldrich, Acros organics, and J&K scientific.

GPC measurements were carried out with a Shimadzu 10A apparatus with a PLgel 5 µm mixed D column. The measurements were done in tetrahydrofurane (THF) as eluent toward poly(styrene) standards. ¹H NMR measurements were done with a Bruker Avance 300 MHz for the monomers, a Bruker Avance 400 MHz for the initiators, and a Bruker Avance 600 MHz for the different polymers. UV-vis and CD spectra were obtained respectively with a Perkin Elmer Lambda 900 and a JASCO J-810 spectrometer. MALDI-ToF mass spectra were acquired on a Waters QToF Premier mass spectrometer equipped with a Nd: YAG laser, operating at 355 nm (third harmonic) with a maximum output of 66.3 µJ per surface unit delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-Flight mass analyses were performed in the reflectron mode at a resolution of about 10k and the samples were analyzed using trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB), as a matrix at 40 mg mL-1 solution in CHCl₃. Polythiophene samples were dissolved in CHCl₃ to obtain 1 mg mL-1 solutions. Aliquots $(1 \mu L)$ of those solutions were applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass all the ions of the distribution, and they were transmitted into the pusher region of the time-of-flight analyser where they were mass analysed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

SYNTHESIS OF THE PRECURSOR MONOMERS

(-)-(R)-2-bromo-5-iodo-3-(3,7-dimethyloctyl)thiophene and (+)-(S)-2-bromo-5-iodo-3-(3,7-dimethyloctyl)thiophene were prepared according to literature procedures¹.

SYNTHESIS OF THE PRECURSOR INITIATORS

Bomo-(o-methylbenzene)-bis(triphenylphosphine)nickel(II) (1)

Precursor initiators 1 was synthezised according to the literature.^{1,2}

Yield 1: 0,7872 g (26%)

Bomo-(o-ethylbenzene)-bis(triphenylphosphine)nickel(II) (2)

A solution of 1-bromo-(2-ethyl)benzene (8,85 mmol; 1,64 g) in dry toluene (150 mL) under N₂ is added to Ni(PPh₃)₄ (6,00 mmol; 6,65 g). The reaction mixture is protected from light and stirred for 15 hours at room temperature. After filtration the solution is concentrated under reduced pressure at 30°C, precipitated in pentane and filtered. The solution is isolated as an orange powder.

Yield 2: 1,82 g (37%)

¹H NMR (400 MHz, CD₂Cl₂) δ: 7,50 (m, 12H); 7,38 (t, 6H); 7,28 (t, 12H); 7,14 (d, 1H); 6,46 (t, 1H); 6,30 (t; 1H); 6,07 (d; 1H); 2,87 (q, 2H); 0,56 (t, 3H, 7,5 Hz)

³¹P NMR (400 MHz, CDCl₃) δ: 21,75 (s)

Bomo-(o-i-propylbenzene)-bis(triphenylphosphine)nickel(II) (3)

A solution of 1-bromo-(2-(i-propyl))benzene (9,00 mmol; 1,79 g) in dry toluene (150 mL) under N_2 is added to Ni(PPh₃)₄ (6,00 mmol; 6,65 g). The reaction mixture is protected from light and stirred for 15 hours at room temperature. After filtration the solution is concentrated under reduced pressure at 30°C, precipitated in pentane and filtered. The solution is isolated as an orange powder.

Yield 3: 2,74 g (50%)

¹H NMR (400 MHz, CD2Cl2) δ: 7,40 (m, 18H); 7,26 (t, 12H); 6,49 (m, 3H); 5,99 (m, 1H); 4,89 (m, 1H); 0,90 (d, 6H, 6,9 Hz)

³¹P NMR (400 MHz, CDCl₃) δ: 19,15 (s)

SYNTHESIS OF THE POLYMERS

M-P1a, E-P1a, *i*P-P1a

An overview of the polymerization of M-P1a, E-P1a and *i*P-P1a can be found in scheme S1.



Scheme S1. Schematic representation of KCTP of polymers **M-P1a**, **E-P1a** and *i***P-P1a** with respectively initiators **In M, In E and In** *i***P.**

(+)-(*S*)-2-bromo-5-iodo-3-(3',7'-dimethyloctyl)thiophene (**4**) (0,525 mmol; 0,225 g) was purged with argon and dissolved in dry THF (4,806 ml). Next, *i*-PrMgCl·LiCl (0,525 mmol; 0,444 mL) was added and the solution was stirred for 30 minutes at room temperature. In the meantime dppp (0,0125 mmol; 5,20 mg) and precursor initiator **1** (0,00625 mmol; 5,10 mg) were purged with argon and dissolved in dry THF (1,5 mL). This reaction mixture was stirred for 15 minutes at room temperature. 5 mL of the obtained (*S*) monomer solution was transferred

to the initiator mixture and stirred at room temperature. The 0,25 mL (*S*) monomer solution left, was quenched with 0,50 mL D₂O for ¹H NMR analysis. After a polymerization time of 90 minutes, the polymerization was terminated with a 2 M HCl in THF solution. This mixture was concentrated under reduced pressure, and the polymer was precipitated in methanol. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated, the polymer was precipitated in methanol, filtered, and dried under reduced pressure. Polymer **M-P1a** was recovered as a dark purple solid.

The same was done in order to obtain polymers **E-P1a** and *i***P-P1a** with respectively precursor initiator **2** and **3**.

Yield: M-P1a: 0,067 g; E-P1a: 0,061 g; *i*P-P1a: 0,059 g

<u>E-P(2-5)a, *i*P-P(2-5)a, E-P(2-5)b, *i*P-P(2-5)b</u>

An overview of the polymerization of **E-P(2-5)a**, *i***P-P(2-5)a**, **E-P(2-5)b** and *i***P-P(2-5)b** can be found in scheme S2.



Scheme S2. Schematic representation of KCTP of polymers **E-P(2-5)a**, *i***P-P(2-5)a**, **E-P(2-5)b** and *i***P-P(2-5)b**.

(+)-(*S*)-2-bromo-5-iodo-3-(3',7'-dimethyloctyl)thiophene (**4**) (2,78 mmol; 1,19 g) was purged with argon and dissolved in dry THF (25,6 ml). Next, *i*-PrMgCl·LiCl (2,78 mmol; 1,26M; 2,20 mL) was added and the solution was stirred for 30 minutes at room temperature. In the meantime dppp and precursor initiator **2** and **3** were divided in different flasks as shown in table S1, purged with argon, and dissolved in dry THF (1,5 mL). These reaction mixtures were stirred for 15 minutes at room temperature. 2 x 4,375 mL, 2 x 3, 750 mL, 2 x 3,125 mL and 2 x 2,500 mL of the (*S*) solution were transferred to the different flasks in order to form the first blocks of the different block copolymers. The 0,25 mL (*S*) monomer solution left, was quenched with 0,50 mL D₂O for ¹H NMR analysis. After a polymerization time of 70 minutes at room temperature, 1/5 of the volume of the different solutions were transferred to separated - with argon purged - flasks and terminated with a 2 M HCl in THF solution in order to respectively

obtain E-P2a, *i*P-P2a, E-P3a, *i*P-P3a, E-P4a, *i*P-P4a, E-P5a and *i*P-P5a. These mixtures were concentrated under reduced pressure, and the polymers were precipitated in methanol. Next, the polymers were filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fractions were concentrated, the polymers were precipitated in methanol, filtered, and dried under reduced pressure. Polymers E-P2a, *i*P-P2a, E-P3a, *i*P-P3a, E-P4a, *i*P-P4a, E-P5a and *i*P-P5a were recovered as dark purple solids.

To the left polymerization solutions (4/5 volume) respectively 2 x 0,50 mL, 2 x 1,00 mL, 2 x 1,50 mL and 2 x 2,00 mL of the (*R*) monomer solution were transferred. This monomer was obtained by reaction of (-)-(*R*)-2-bromo-5-iodo-3-(3',7'-dimethyloctyl)thiophene (**5**) (1,03 mmol; 0,440 g) with *i*-PrMgCl·LiCl (1,03 mmol; 1,26M; 0,81 mL) in dry THF for 30 minutes. The 0,25 mL (*R*) monomer solution left, was quenched with 0,50 mL D₂O for ¹H NMR analysis. The polymerization mixtures are stirred at room temperature. After 45 minutes the solutions of **E-P2b** and *i***P-P2b** were terminated with a 2 M HCl in THF solution. The same was done for **E-P3b** and *i***P-P3b** 30 minutes later and again for **E-P4a** and *i***P-P4a** 15 minutes later. After a polymerization time of 120 minutes also **E-P5a** and *i***P-P5a** were terminated with a 2 M HCl in THF solution. The different mixtures were concentrated under reduced pressure, and the polymers were precipitated in methanol. Next, the polymers were filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fractions were concentrated, the polymers were precipitated in methanol, filtered, and dried under reduced pressure. Polymers **E-P2b**, *i***P-P2b**, *E-P3b*, *i***P-P3b**, *E-P4b*, *i***P-P4b**, *E-P5b* and *i***P-P5b** were recovered as dark purple solids.

Yield: **E-P2b**: 64 mg; *i***P-P2b**: 68,4 mg; **E-P3b**: 67,9 mg; *i***P-P3b**: 77,4 mg; **E-P4b**: 66,9 mg; *i***P-P4b**: 70,3 mg; **E-P5b**: 66,3 mg; *i***P-P5b**: 59,4 mg Table S1. Overview amounts of precursor initiator **2**, precursor initiator **3** and dppp used for the polymerization of **E-P2b**, *i***P-P2b**, **E-P3b**, *i***P-P3b**, **E-P4b**, *i***P-P4b**, **E-P5b** and *i***P-P5b**.

Polymer	2 (g; mmol)	3 (g; mmol)	Dppp (g; mmol)
E-P2b	0.0103; 0.0125	/	0.0103; 0.0250
<i>i</i> P-P2b	0.0103; 0.0125	/	0.0103; 0.0250
E-P3b	0.0103; 0.0125	/	0.0103; 0.0250
<i>i</i> P-P3b	0.0103; 0.0125	/	0.0103; 0.0250
E-P4b	/	0.0115; 0.0125	0.0103; 0.0250
<i>i</i> P-P4b	/	0.0115; 0.0125	0.0103; 0.0250
E-P5b	/	0.0115; 0.0125	0.0103; 0.0250
<i>i</i> P-P5b	/	0.0115; 0.0125	0.0103; 0.0250

<u>M-P(2-5)a, M-P(2-5)b</u>

An overview of the polymerization of **M-P(2-5)a** and **M-P(2-5)b** can be found in scheme S2. The polymerization proceeds as for **E-P(2-5)a**, *i***P-P(2-5)a**, **E-P(2-5)b** and *i***P-P(2-5)b** but with the amounts as shown in table S2.

Table S2. Overview amounts of monomer (*S*), monomer (*R*), precursor initiator 1 and dppp used for the synthesis of M-P2b, M-P3b, M-P4b and M-P5b.

Polymer	Monomer (S)	Monomer (R)	1	Dppp
	(mmol)	(mmol)	(mmol; g)	(mmol; g)
M-P2b	0.875	0.100	(0.025; 0.0189)	(0.050; 0.0206)
M-P3b	0.750	0.200	(0.025; 0.0189)	(0.050; 0.0206)
M-P4b	0.625	0.300	(0.025; 0.0189)	(0.050; 0.0206)

M-P5b	0.500	0.400	(0.025; 0.0189)	(0.050; 0.0206)

Yield: M-P2b: 139,9 mg; M-P3b: 109,9 mg; M-P4b: 127,7 mg; M-P5b: 171,6 mg

¹H NMR SPECTRA OF THE PRECURSOR INITIATORS

Bomo-(o-ethylbenzene)-bis(triphenylphosphine)nickel(II) (2)



Figure S1. ¹H NMR spectrum of Bomo-(*o*-ethylbenzene)-bis(triphenylphosphine)nickel(II) (**2**) in CD₂Cl₂.

Bomo-(*o-i*-propylbenzene)-bis(triphenylphosphine)nickel(II) (**3**)



Figure S2. ¹H NMR spectrum of Bomo-(*o-i*-propylbenzene)-bis(triphenylphosphine)nickel(II) (**3**) in CD₂Cl₂.

³¹P NMR SPECTRA OF THE PRECURSOR INITIATORS

Bomo-(*o*-ethylbenzene)-bis(triphenylphosphine)nickel(II) (2)



Figure S3. ³¹P NMR spectrum of Bomo-(*o*-ethylbenzene)-bis(triphenylphosphine)nickel(II) (2) in CDCl₃.

Bomo-(*o-i*-propylbenzene)-bis(triphenylphosphine)nickel(II) (**3**)



Figure S4. ³¹P NMR spectrum of Bomo-(*o-i*-propylbenzene)-bis(triphenylphosphine)nickel(II) (**3**) in CDCl₃.

¹H NMR SPECTRA OF THE POLYMERS

M-P1a



Figure S5. ¹H NMR spectrum of **M-P1a** in CDCl₃.











Figure S7. ¹H NMR spectrum of **M-P2b** in CDCl₃.



Figure S8. ¹H NMR spectrum of **M-P3a** in CDCl₃.





Figure S9. ¹H NMR spectrum of **M-P3b** in CDCl₃.



Figure S10. ¹H NMR spectrum of **M-P4a** in CDCl₃.





Figure S11. ¹H NMR spectrum of **M-P4b** in CDCl₃.



Figure S12. ¹H NMR spectrum of **M-P5a** in CDCl₃.

M-P5b



Figure S13. ¹H NMR spectrum of **M-P5b** in CDCl₃.



Figure S14. ¹H NMR spectrum of **E-P1a** in CDCl₃.

E-P2a



Figure S15. ¹H NMR spectrum of **E-P2a** in CDCl₃.











Figure S17. ¹H NMR spectrum of **E-P3a** in CDCl₃.





Figure S18. ¹H NMR spectrum of **E-P3b** in CDCl₃.





Figure S19. ¹H NMR spectrum of **E-P4a** in CDCl₃.



Figure S20. ¹H NMR spectrum of **E-P4b** in CDCl₃.





Figure S21. ¹H NMR spectrum of **E-P5a** in CDCl₃.



Figure S22. ¹H NMR spectrum of **E-P5b** in CDCl₃.



Figure S23. ¹H NMR spectrum of *i***P-P1a** in CDCl₃.



Figure S24. ¹H NMR spectrum of *i***P-P2a** in CDCl₃.





Figure S25. ¹H NMR spectrum of *i***P-P2b** in CDCl₃.



Figure S26. ¹H NMR spectrum of *i***P-P3a** in CDCl₃.

*i*P-P3b



Figure S27. ¹H NMR spectrum of *i***P-P3b** in CDCl₃.





Figure S29. ¹H NMR spectrum of *i***P-P4b** in CDCl₃.

[ppm]



Figure S30. ¹H NMR spectrum of *i***P-P5a** in CDCl₃.





Figure S31. ¹H NMR spectrum of *i***P-P5b** in CDCl₃.

CD SPECTRA

The influence of the end-group of the self-assembly of the different polymer series is analyzed using CD spectroscopy. First the polymers are solubilized in CHCl₃. Upon the addition of about methanol (MeOH) the polymers start to stack.





Figure S32. CD spectrum of M-P1a in CHCl₃ upon addition of methanol (MeOH).







series 3



Figure S34. CD spectrum of M-P1a in CHCl₃ upon addition of methanol (MeOH).

M-P2b (8% (R)-chiral monomer)



Figure S35. CD spectrum of M-P2b in CHCl₃ upon addition of methanol (MeOH).





Figure S36. CD spectrum of M-P2b in CHCl₃ upon addition of methanol (MeOH).





Figure S37. CD spectrum of M-P2b in CHCl₃ upon addition of methanol (MeOH).

<u>M-P3b (23% (*R*)-chiral monomer)</u>





Figure S38. CD spectrum of M-P3b in CHCl₃ upon addition of methanol (MeOH).





Figure S39. CD spectrum of **M-P3b** in CHCl₃ upon addition of methanol (MeOH).

series 3



Figure S40. CD spectrum of M-P3b in CHCl₃ upon addition of methanol (MeOH).



Figure S41. CD spectrum of M-P4b in CHCl₃ upon addition of methanol (MeOH).





Figure S42. CD spectrum of M-P4b in CHCl₃ upon addition of methanol (MeOH).





Figure S43. CD spectrum of M-P4b in CHCl₃ upon addition of methanol (MeOH).

<u>M-P5b (50% (*R*)-chiral monomer)</u>



Figure S44. CD spectrum of M-P5b in CHCl₃ upon addition of methanol (MeOH).





Figure S45. CD spectrum of **M-P5b** in CHCl₃ upon addition of methanol (MeOH). series **3**



Figure S46. CD spectrum of M-P5b in CHCl₃ upon addition of methanol (MeOH).





Figure S47. CD spectrum of E-P1a in CHCl₃ upon addition of methanol (MeOH).



Figure S48. CD spectrum of E-P1a in CHCl₃ upon addition of methanol (MeOH).













Figure S50. CD spectrum of E-P2b in CHCl₃ upon addition of methanol (MeOH).





Figure S51. CD spectrum of E-P2b in CHCl₃ upon addition of methanol (MeOH).

series 3



Figure S52. CD spectrum of \mathbf{E} -P2b in CHCl₃ upon addition of methanol (MeOH).





Figure S53. CD spectrum of E-P3b in CHCl₃ upon addition of methanol (MeOH).





Figure S54. CD spectrum of E-P3b in CHCl₃ upon addition of methanol (MeOH).





Figure S55. CD spectrum of **E-P3b** in CHCl₃ upon addition of methanol (MeOH).







Figure S56. CD spectrum of E-P4b in CHCl₃ upon addition of methanol (MeOH).





Figure S57. CD spectrum of **E-P4b** in CHCl₃ upon addition of methanol (MeOH).





Figure S58. CD spectrum of E-P4b in CHCl₃ upon addition of methanol (MeOH).





Figure S59. CD spectrum of E-P5b in CHCl₃ upon addition of methanol (MeOH).





Figure S60. CD spectrum of E-P5b in CHCl₃ upon addition of methanol (MeOH).





Figure S61. CD spectrum of E-P5b in CHCl₃ upon addition of methanol (MeOH).

iP-P1a (0% (R)-chiral monomer)





Figure S62. CD spectrum of *i***P**-**P1a** in CHCl₃ upon addition of methanol (MeOH).





Figure S63. CD spectrum of *i***P-P1a** in CHCl₃ upon addition of methanol (MeOH).

series 3



Figure S64. CD spectrum of *i***P**-**P1a** in CHCl₃ upon addition of methanol (MeOH).





Figure S65. CD spectrum of *i***P-P2b** in CHCl₃ upon addition of methanol (MeOH).





Figure S66. CD spectrum of *i***P**-**P2b** in CHCl₃ upon addition of methanol (MeOH).





Figure S67. CD spectrum of *i***P-P2b** in CHCl₃ upon addition of methanol (MeOH).

*i***P-P3b** (15% (*R*)-chiral monomer)





Figure S68. CD spectrum of *i***P-P3b** in CHCl₃ upon addition of methanol (MeOH).





Figure S69. CD spectrum of *i***P-P3b** in CHCl₃ upon addition of methanol (MeOH).

series 3



Figure S70. CD spectrum of *i***P-P3b** in CHCl₃ upon addition of methanol (MeOH).





Figure S71. CD spectrum of *i***P**-**P4b** in CHCl₃ upon addition of methanol (MeOH).





Figure S72. CD spectrum of *i*P-P4b in CHCl₃ upon addition of methanol (MeOH).





Figure S73. CD spectrum of *i***P**-**P**4b in CHCl₃ upon addition of methanol (MeOH).

*i***P-P5b** (39% (*R*)-chiral monomer)





Figure S74. CD spectrum of *i***P-P5b** in CHCl₃ upon addition of methanol (MeOH).





Figure S75. CD spectrum of *i***P-P5b** in CHCl₃ upon addition of methanol (MeOH).





Figure S76. CD spectrum of *i***P-P5b** in CHCl₃ upon addition of methanol (MeOH).



Figure S77. $\Delta \varepsilon$ at a 45% methanol content plotted for the three different polymer series (**M-P1a, M-P(2-5)b**; **E-P1a, E-P(2-5)b**; *i***P-P1a**, *i***P(2-5)b**) in function of the wavelength.

MALDI-TOF SPECTRA OF THE POLYMERS

M-P1a



Figure S78. MALDI-ToF spectrum of M-P1a.



Figure S79. MALDI-ToF spectrum of M-P1a.





QTOF1_KOECKELBERGHS_1M_150217_001_106 (1.802) Sm (SG, 10x6.00); Cm (9:152)



Figure S80. MALDI-ToF spectrum of M-P2b.



Figure S81. MALDI-ToF spectrum of M-P2b.

M-P3b



Figure S82. MALDI-ToF spectrum of M-P3b.



Figure S83. MALDI-ToF spectrum of **M-P3b**.

M-P4b



Figure S84. MALDI-ToF spectrum of M-P4b.



Figure S85. MALDI-ToF spectrum of M-P4b.



Figure S86 MALDI-ToF spectrum of M-P5b.



Figure S87. MALDI-ToF spectrum of M-P5b.

E-P1a



Figure S88. MALDI-ToF spectrum of **E-P1a**.



Figure S89. MALDI-ToF spectrum of E-P1a.

E-P2b



Figure S90. MALDI-ToF spectrum of **E-P2b**.



Figure S91. MALDI-ToF spectrum of E-P2b.



0------ m/z

Figure S93. MALDI-ToF spectrum of **E-P3b**.



Figure S95. MALDI-ToF spectrum of **E-P4b**.



Figure S97. MALDI-ToF spectrum of E-P5b.

*i*P-P1a



Figure S98. MALDI-ToF spectrum of *i***P-P1a**.



Figure S99. MALDI-ToF spectrum of *i*P-P1a.





Figure S103. MALDI-ToF spectrum of *i***P-P3b**.

*i*P-P4b



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