Supporting Information

The Controlled Synthesis of a Helical, Conjugated Polythiophene

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Experimental Information

All reagents were purchased from TCI, Sigma-Aldrich, J&K Scientific and Acros Organics and used without further purification. 2,2,6,6-Tetramethylpiperidinylmagnesium chloride lithium chloride complex was titrated before use according to the procedure by Love *et al.*[1] Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. ^{13}C-NMR-spectra were measured on a Bruker Avance 600 MHz-spectrometer. Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 10A GPC system. The flow rate is 1 ml/min. The column is a PLgel 5 µm mixed-D type column which is kept at a temperature of 30°C, and the detection system consists of a differential refractometer and a UV−vis spectrophotometer. The GPC system is calibrated toward 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. UV−vis and CD measurements were performed on a Varian 400 Scan and a Jasco J-1500, respectively. Compounds **1**, **2a**[2], **2b**[3], **6a**[4], **6b**[5]**, 10**[6] and **12b**[7] were prepared according to literature procedures.

Synthesis of the monomers

Synthesis of 3a. NaH (8.80 mmol, 211 mg) was suspended in 20 ml of dry THF under N_2-atmosphere. **2a** (8.80 mmol, 4.32g) was dissolved under N_2-atmosphere in 10 ml of dry THF and added dropwise to the stirring suspension. Compound **1** (8.00 mmol, 2.51g) was dissolved under N_2-atmosphere in 20 ml of dry THF and added dropwise to the stirring suspension. The suspension was then heated to reflux for 2 hours, after which aqueous HCl (1M) was added. The product was extracted with DCM and the organic layer was washed with a saturated $NaHCO_3$-solution and a saturated NaCl-solution. The organic layers were then dried on $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography and a colorless viscous oil was obtained which crystallized upon standing. (SiO_2; eluent: heptane/DCM (7/3)). Yield: 4.22 g (74%). Melting point: 29-30°C ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.25 (d, 1H, 6 Hz), 7.19 (d, 1H, 6 Hz), 6.95 (d, 1H, 16 Hz), 6.87 (d, 1H, 16 Hz) 6.7 (s, 2H), 4.06-3.94 (m, 6H), 1.88-1.68 (m, 6H), 1.53-1.41 (m, 6H), 1.40-1.21 (m, 24H), 0.88 (m, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 153.4, 138.7, 138.3, 132.2, 130.9, 126.0, 124.7, 120.0, 110.9, 105.4, 73.6, 69.3, 31.9, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 22.6, 14.1; MS (ESI) (m/z): 648.2

Synthesis of 3b. The same procedure as described for **3a** was followed, using **2b** (5.50 mmol, 2.70 g) instead of **2a**. The product was isolated as colorless, viscous oil. Yield: 0.57 g (15%). ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.25 (d, 1H,6 Hz), 7.19 (d, 1H, 6 Hz), 6.95 (d, 1H,16 Hz), 6.87 (d, 1H, 16 Hz), 6.7 (s, 2H), 4.13-3.92 (m, 6H), 1.95-1.80 (m, 3H), 1.78-1.68 (m, 3H), 1.67-1.45 (m, 6H), 1.41-1.23 (m, 9H), 1.23-1.04 (m, 9H), 0.97-0.90 (m, 9H), 0.89-0.82 (m, 18H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 153.4, 138.7, 138.3, 132.2, 130.9, 126.0, 124.7, 120.0, 110.9, 105.4, 71.8, 67.6, 39.4, 39.3, 37.6, 37.4, 37.4; 36.5, 29.9, 29.7, 28.0, 24.8, 24.7, 22.7, 22.6, 22.5, 19.7, 19.6; MS (ESI) (m/z): 733.2

Synthesis of 4a. **3a** (5.40 mmol, 3.53 g) was dissolved in DCM and I_2 (2.70 mmol, 0.690 g) and (diacetoxyiodo)benzene (2.70 mmol, 0.8700 g) were added. The reaction was then stirred overnight under N_2-atmosphere. A $Na_2S_2O_3$-solution was then added and the organic layer was separated and washed with a saturated NaCl-solution. The solvent was removed under reduced pressure and the crude product was purified by column chromatography. The product was obtained as a colorless viscous oil. (SiO_2; eluent: heptane/DCM (7/3)). Yield: 3.56 g (85%). ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.28 (s, 2H), 7.25 (d, 1H, 16 Hz), 6.98 (s, 1H), 6.81 (d, 1H, 16 Hz), 4.07-3.94 (m, 6H), 1.91-1.69 (m, 6H), 1.52-1.43 (m, 6H), 1.52-1.21 (m, 24H), 0.88 (m, 9H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 153.8, 152.9, 141.7, 138.0, 135.6, 134.9, 126.2, 125.0, 122.7, 111.6, 106.5, 89.4, 74.0, 73.8, 69.1, 31.9, 31.8, 30.3, 30.2, 29.5, 29.5, 29.4, 29.36, 29.33, 29.30, 26.2, 26.1, 26.0, 22.7, 14.1; MS (ESI) (m/z): 776.2

Synthesis of 7a. A flask was charged with **6a** (12.1 mmol, 7.10 g), 3-thienylboronic acid (24.2 mmol, 3.10 g), K_2CO_3 (84.7 mmol, 11.7 g) and a catalytic amount of aliquat 336; 70 ml of toluene, 35 ml of THF and 16 ml of water were added. The resulting mixture was degassed and brought under N_2-atmosphere. $Pd(PPh_3)_4$ (363 µmol, 420 mg) was then added and the mixture was heated to reflux for 24 hours. Toluene and THF were removed under reduced pressure and the product was extracted with ethyl acetate. The organic layers were washed with a saturated NaCl-solution and dried on $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography. The product was isolated as a colorless viscous oil which crystallized upon standing. (SiO_2; eluent: heptane/DCM (8/2)). Yield: 5.90 g (89%). Melting point: 35-36°C ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.38-7.29 (m, 3H), 6.76 (s, 2H), 4.06-3.92 (m, 6H), 1.88-1.69 (m, 6H), 1.53-1.41 (m, 6H), 1.41-1.20 (m, 24H), 0.88 (m, 6H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 153.4, 142.7, 137.9, 131.3, 126.5, 126.0, 119.8, 105.6, 73.5, 69.3, 31.9, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7, 22.6, 14.1; MS (ESI) (m/z): 544.3

Synthesis of 7b. The same procedure as described for **7a** was followed, using **6b** (4.80 mmol, 3.25 g) instead of **6a**. The product was isolated as a colorless, viscous oil. Yield: 2.58 g (85%) ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.39-7.31 (m, 3H), 6.77 (s, 2H), 4.13-3.92 (m, 6H), 1.95-1.80 (m, 3H), 1.78-1.68 (m, 3H), 1.67-1.45 (m, 6H), 1.41-1.23 (m, 9H), 1.23-1.04 (m, 9H), 0.97-0.90 (m, 9H), 0.89-0.82 (m, 18H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 153.4, 142.7, 137.9, 131.3, 126.5, 126.0, 119.8, 105.6, 71.9, 67.6, 39.4, 39.3, 37.6, 37.4, 36.5, 29.9, 29.8, 28.0, 24.8, 24.7, 22.7, 22.6, 22.6, 19.6; MS (ESI) (m/z): 628.2

Synthesis of 8a. **7a** (12.4 mmol, 6.75 g) was dissolved in THF and shielded from light. The flask was cooled to 0°C and NBS (12.4 mmol, 2.21 g) was slowly added. The reaction mixture was stirred overnight at room temperature. A $Na_2S_2O_3$-solution was added and the product was extracted with diethyl ether. The organic layer was washed with a saturated $NaHCO_3$-solution and a saturated NaCl-solution. The organic layer was dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography and isolated as a colorless viscous oil. (SiO_2; eluent: heptane/DCM (8/2)). Yield: 3.95 g (45%). ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.28 (d, 1H, 5.5 Hz), 7.01 (d, 1H, 5.5 Hz), 6.72 (s, 2H), 4.04-3.95 (m, 6H), 1.88-1.69 (m, 6H), 1.53-1.41 (m, 6H), 1.41-1.20 (m, 24H), 0.88 (m, 6H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 152.9, 141.2, 137.9, 129.9; 129.2, 125.7, 108.1, 107.5, 73.5, 69.2, 31.9, 31.8, 30.4, 29.6, 29.4, 29.39, 29.31, 26.12, 22.7, 22.6, 14.1; MS (ESI) (m/z): 625.4

Synthesis of 8b. The same procedure as described for **8a** was followed, using **7b** (4.10 mmol, 2.58 g) instead of **7a**. The product was isolated as colorless, viscous oil. Yield: 1.46 g (51%) ^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 7.29 (d, 1H, 5.5 Hz), 7.02 (d, 1H, 5.5 Hz), 6.73 (s, 2H), 4.11-3.94 (m, 6H), 1.95-1.80 (m, 3H), 1.78-1.68 (m, 3H), 1.67-1.45 (m, 6H), 1.41-1.23 (m, 9H), 1.23-1.04 (m, 9H), 0.97-0.90 (m, 9H), 0.89-0.82 (m, 18H) ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm) = 152.9, 141.2, 137.9, 129.9, 129.2, 125.7, 108.1, 107.5, 71.8, 67.5, 39.4, 39.3, 37.6, 37.4, 36.4, 29.9, 29.8, 28.0, 24.8, 22.7, 22.6, 19.6; MS (ESI) (m/z): 707.5

Attempted synthesis of 2-bromo-5-iodo-3-(3,4,5-tris(octyloxy)phenyl)thiophene. **8a** (0.50 mmol, 0.312 g) was dissolved in DCM and shielded from light. I_2 (0.25mmol, 0.064g) and (diacetoxyiodo)benzene (0.25 mmol, 0.081g) were added and the resulting mixture was stirred overnight. ^{1}H-NMR analysis revealed the formation of 2-bromo-3-(2-iodo-3,4,5-tris(octyloxy)phenyl)thiophene. Since the desired product was not formed, no further purification was done.

Synthesis of the polymers

Procedure for the synthesis of polymer P1 A flask was charged with **3a** (0.250 mmol, 163 mg) and purged with N_2. 2,2,6,6-Tetramethylpiperidinylmagnesium chloride lithium chloride complex (TMPMgCl.LiCl) (0.250 mmol, 0.250 ml, 1M) was added and the mixture was stirred for 3 hours at room temperature. **10** (12.5 µmol, 10.7 mg) and 1,3-bis(diphenylphosphino)propane (dppp) (25 µmol, 10.3 mg) were added to another flask and purged with N_2, dry THF (1 ml) was added and the resulting mixture was stirred for 15 minutes. The monomer solution was then diluted with 2.5 ml of dry THF (to reduce viscosity) and transferred to the initiator solution. After one hour of stirring at room temperature, a few drops of acidified THF were added and the resulting mixture was precipitated in MeOH. The polymer was filtered in a Soxhlet thimble and purified by Soxhlet extraction with MeOH and $CHCl_3$. The $CHCl_3$-fraction was concentrated and precipitated in MeOH. The polymer was filtered on a glass sintered filter and dried under reduced pressure. Yield: 68.8 mg (48%)

Procedure for the synthesis of polymer P2 The same procedure as for **P1** was followed, using **3b** instead of **3a**. Yield: 84.8 mg (52%)

Procedure for the synthesis of polymer P3 The same procedure as for **P1** was followed, using **8a** instead of **3a**. Yield: 53.5 mg (39%)

Procedure for the synthesis of polymer P3 The same procedure as for **P1** was followed, using **8b** instead of **3a**. Yield: 77.6 mg (49%)

Procedure for the synthesis of polymer P5a and block copolymer P5b

3a (0.25 mmol,0.163 g) was brought under N_2-atmosphere. TMPMgCl.LiCl (0.25 mmol, 0.31 ml) was added and the resulting mixture was stirred for 3 hours at room temperature. (*S*)-2-bromo-5-iodo-3-(3,7- dimethyloctyl)thiophene (**12b**) (0.375 mmol, 0.161 g) was brought under N_2-atmosphere and *i*-PrMgCl.LiCl (0.375 mmol, 0.290 ml) was added. The mixture was then diluted to 3.75 ml with dry THF. **10** (17.5 µmol, 16.4 mg) and dppp (35 µmol, 14.4 mg) were dissolved in dry THF (1 ml) and stirred for 15 minutes. 3.5 ml of the GRIM reaction was then added. The remaining 0.25 ml was quenched with D_2O for ^{1}H-NMR-analysis. After 1 hour, 1.3 ml of the polymerization solution was brought in another flask and terminated with acidified THF, obtaining polymer **P5a**. The mixture of **3a** and TMPMgCl.LiCl was then diluted to 2.5 ml (to reduce viscosity) and added to the polymerization. The polymerization was terminated after 2 hours by addition of acidified THF. The polymer was then precipitated in MeOH and filtered in a Soxhlet thimble. The polymer was purified by Soxhlet extraction with respectively MeOH and $CHCl_3$. The $CHCl_3$-fraction was concentrated in vacuo and precipitated in MeOH. The polymer was filtered on a glass sintered filter and dried under reduced pressure. Yield: 64.5 mg (59%)

Procedure for the synthesis of polymer P6a and block copolymer P6b

The same procedure as for **P5a** and **P5b** was followed, using **3b** instead of **3a** and **12a** instead of **12b**. Yield: 231 mg (97%)

Procedure for the variation of the degree of polymerization of PVPT

3a (0.54 mmol, 0.3503g) was brought under N_2-atmosphere and TMPMgCl.LiCl (0.54 mmol, 0.67 ml) was added. The mixture was stirred at room temperature for 3 hours and then diluted with dry THF to 6 ml. In another flask, **10** (36.9 µmol, 34.6 mg) and dppp (73.8 µmol, 30.4 mg) were dissolved in 5 ml of dry THF under N_2-atmosphere and stirred for 15 min. This solution was divided in 6 flasks (see Table S1) and 1 ml of the monomer solution was added to each flask. The polymerizations were stirred for 90 min and terminated with acidified THF. Only part of the final polymerization with $\frac{[M]}{[I]} = 100$ was terminated. The remaining part was stirred for an additional 30 minutes before addition of acidified THF to verify that the polymerization was completely finished. The molar mass was equal after 90 and 120 minutes, which indicates the polymerization was finished.

Table S1. Initiator amounts and GPC results of the variation of degree of polymerization

$\frac{[M]}{[I]}$	Amount of initiator solution (ml)	M_n (kg/mol)	Đ
5	2.4	2.0	1.1
10	1.2	2.6	1.1
20	0.6	3.4	1.1
30	0.36	4.9	1.1
50	0.24	6.5	1.1
100	0.12	11.0	1.3

Procedure for the chain extension experiment of the polymerization of P3PVT

3a (0.25 mmol, 0.1625g) was brought under N_2-atmosphere and TMPMgCl.LiCl (0.25 mmol, 0.31 ml) was added. The mixture was stirred at room temperature for 3 hours. **10** (4.2 µmol, 3.9 mg) and dppp (8.4 µmol, 3.5 mg) were dissolved in dry THF (0.5ml) and stirred for 15 minutes. The monomer solution was diluted with dry THF to 2.5 ml. 1.25 ml of this solution was canulated to the initiator solution. The resulting polymerization was stirred for 90 min. Then, 0.3 ml of the polymer solution was cannulated to another flask and terminated with acidified THF and the remainder of the monomer solution was added to the polymerization. The polymerization was stirred for 2 hours and terminated with acidified THF.

Table S2. GPC results of the chain extension experiment

	M_n (kg/mol)	Đ
Before chain extension	6.5	1.1
After chain extension	9.7	1.1

Procedure for the variation of the degree of polymerization of P3PT

The same procedure as for **P3PVT** was followed using **8a** instead of **3a**. GPC results are summarized in table S3.

Table S3 Initiator amounts and GPC results of the variation of degree of polymerization

$\frac{[M]}{[I]}$	Amount of initiator solution (ml)	M_n (kg/mol)	Đ
5	2.4	1.0	1.1
10	1.2	1.6	1.2
20	0.60	2.2	1.2
30	0.36	2.7	1.2
50	0.24	4.3	1.2
100	0.12	6.20	1.3

Procedure for the chain extension experiment of the polymerization of P3PT

The same procedure as for **P3PVT** was followed using **8a** instead of **3a**. GPC results are summarized in table S4.

Table S4 GPC results of the chain extension experiment

	M_n (kg/mol)	Đ
Before chain extension	2.2	1.2
After chain extension	3.2	1.2

GRIM-test of compound 4a

1 equivalent of *i*-PrMgCl.LiCl was added to a solution of **4a** in dry THF. The resulting mixture was stirred at 0°C for 30 minutes after which water was added. The products were extracted with diethyl ether and the solvent was evaporated.

The NMR spectrum of this product (Figure S1) clearly shows several unwanted byproducts. A 'clean' GRIM reaction of compound **4a** (red) quenched with water should result in compound **3a** (green).

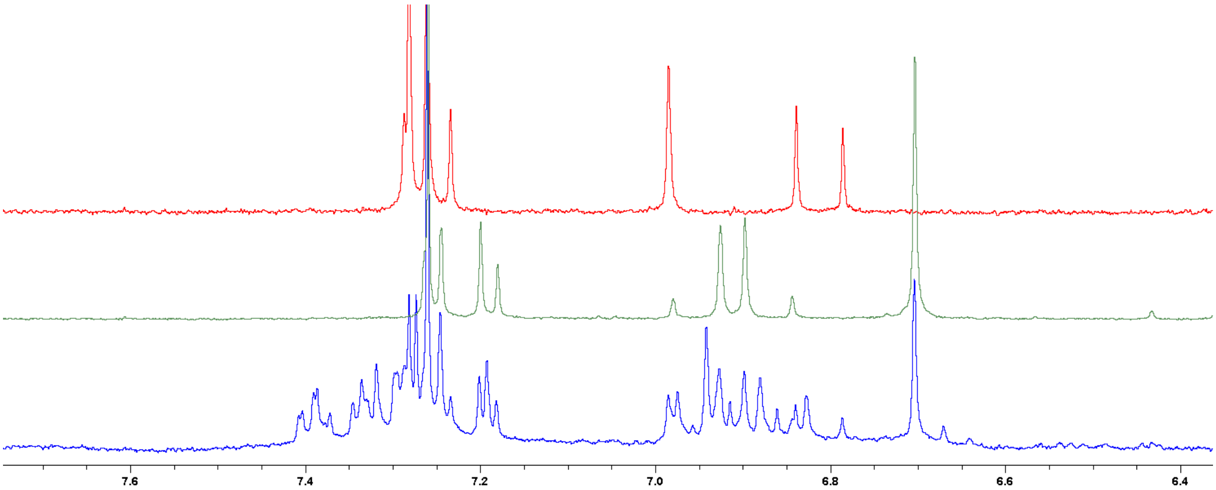

*Figure S1. NMR-spectra of the product of the GRIM-test reaction of compound **4a** (blue), compound **4a** (red) and compound **3a** (green), only the aromatic region is shown as the byproducts are more clearly visible there*

Test reaction of **3a** with TMPMgCl.LiCl

1 equivalent of TMPMgCl.LiCl was added to **3a** under inert atmosphere. The resulting mixture was stirred for 3 hours at room temperature, after which water was added. The product was extracted with diethyl ether and the solvent was evaporated. Compound **3a** was recuperated after reaction.

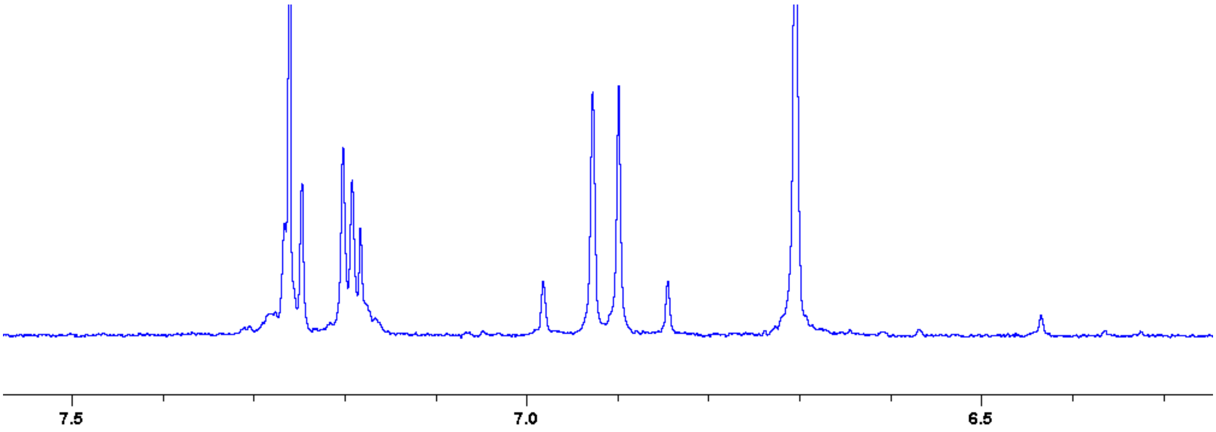

*Figure S2. NMR-spectrum of water-quenched C-H-functionalization of **3a**. Only the aromatic region is shown. The signal at 7.26 ppm arises from residual CHCl$_3$ present in the NMR solvent.*

Test reaction of 8**a** with TMPMgCl.LiCl

1 equivalent of TMPMgCl.LiCl was added to **8a** under inert atmosphere. The resulting mixture was stirred for 3 hours at room temperature, after which water was added. The product was extracted with diethyl ether and the solvent was evaporated. Compound 8**a** was recuperated after reaction.

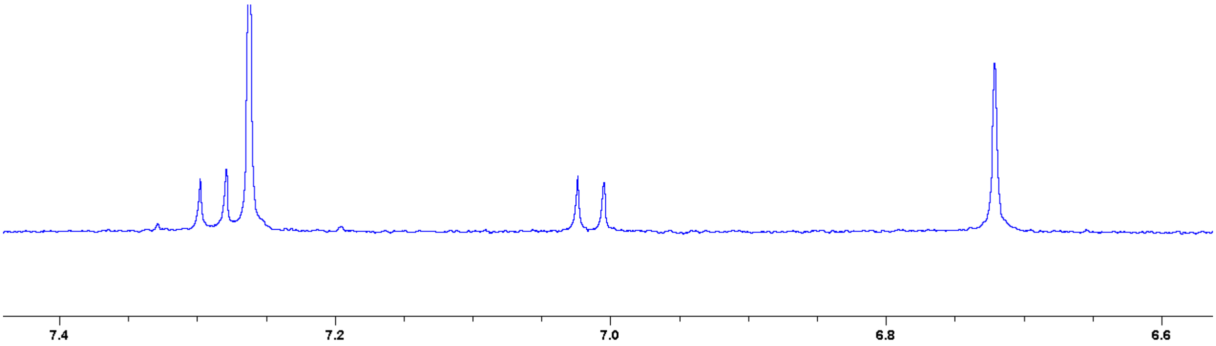

*Figure S3. NMR-spectrum of water-quenched C-H-functionalization of **8a**. Only the aromatic region is shown. The signal at 7.26 ppm arises from residual CHCl$_3$ present in the NMR solvent.*

Polymerization of P3PVT-P3AT block copolymers

Procedure for the synthesis of block copolymer P5b

3a (0.25 mmol,0.163 g) was brought under N$_2$-atmosphere. TMPMgCl.LiCl (0.25 mmol, 0.31 ml) was added and the resulting mixture was stirred for 3 hours at room temperature. **10** (17.5 µmol, 16.4 mg) and dppp (35 µmol, 14.4 mg) were dissolved in dry THF (1 ml) and stirred for 15 minutes. The mixture of **3a** and TMPMgCl.LiCl was then diluted to 2.5 ml and added to the initiator and stirred for one hour. (*S*)-2-bromo-5-iodo-3-(3,7- dimethyloctyl)thiophene (0.375 mmol, 0.161 g) was brought under N$_2$-atmosphere and *i*PrMgCl.LiCl (0.375 mmol, 0.290 ml) was added. The mixture was then diluted to 3.75 ml with dry THF and stirred for 30 minutes. After 1 hour, 1.3 ml of the polymerization solution was brought in another flask and terminated with acidified THF. 3.5ml of the GRIM-reaction was then added to the polymerization. The remaining 0.25 ml was quenched with D_2O for ^{1}H-NMR-analysis. The polymerization was terminated after 2 hours by addition of acidified THF. The GPC results shows that the P3AT block was barely built in.

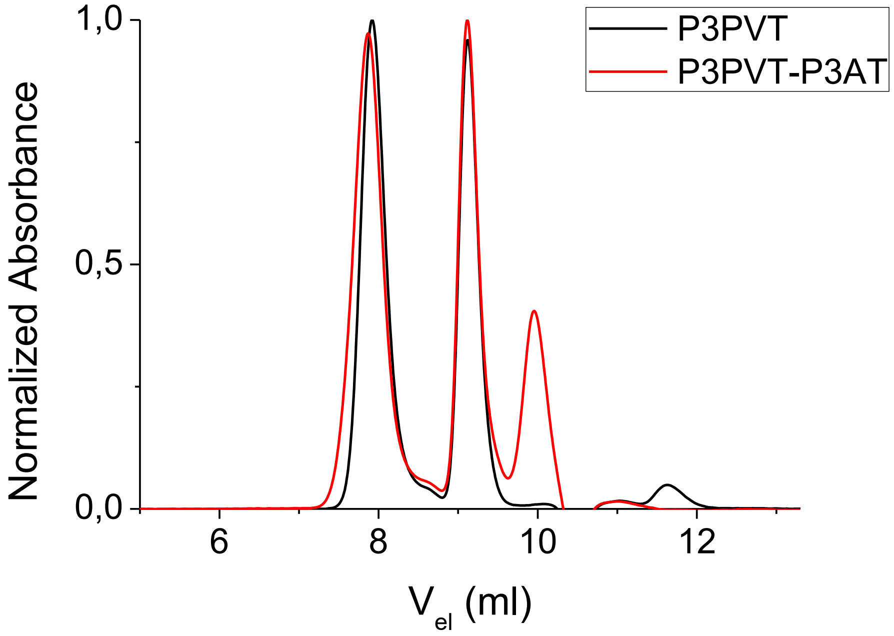

Figure S4. GPC-spectra of the P3PVT-P3AT block copolymer. The peak at 9.5 ml belongs to the 3-PVT monomer, the peak at 10 ml to the 3-alkylthiophene monomer.

NMR spectra

All spectra were recorded in $CDCl_3$ with 0.1 v/v TMS, 300 MHz.

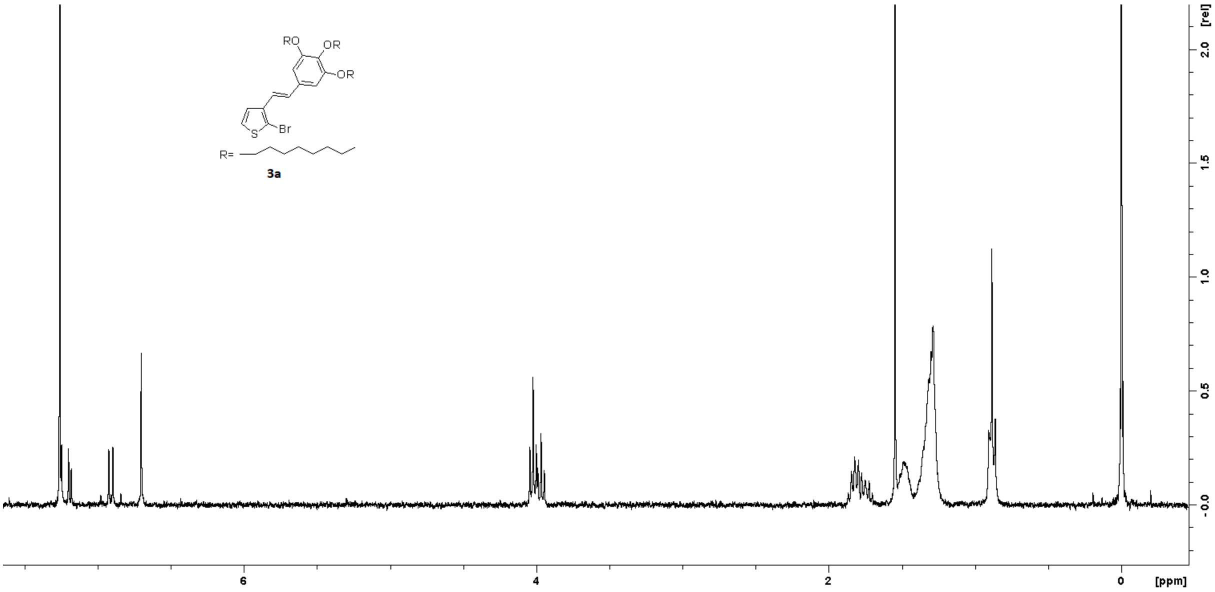

*Figure S 5. ^{1}H-NMR-spectrum of compound **3a.***

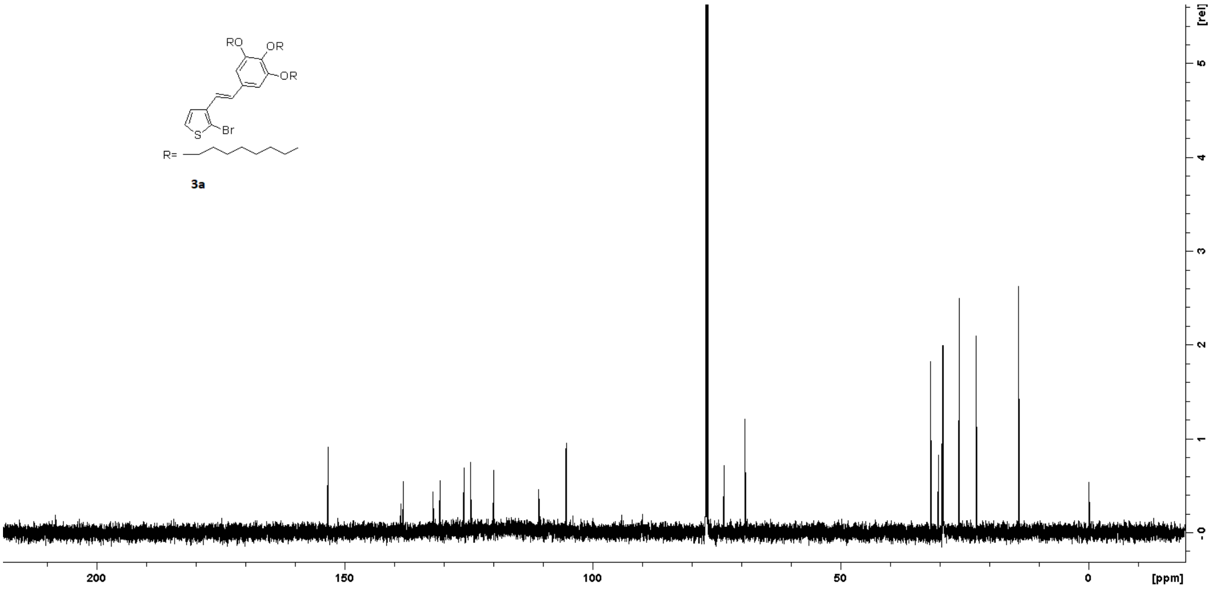

*Figure S 6. ^{13}C-NMR spectrum of compound **3a**.*

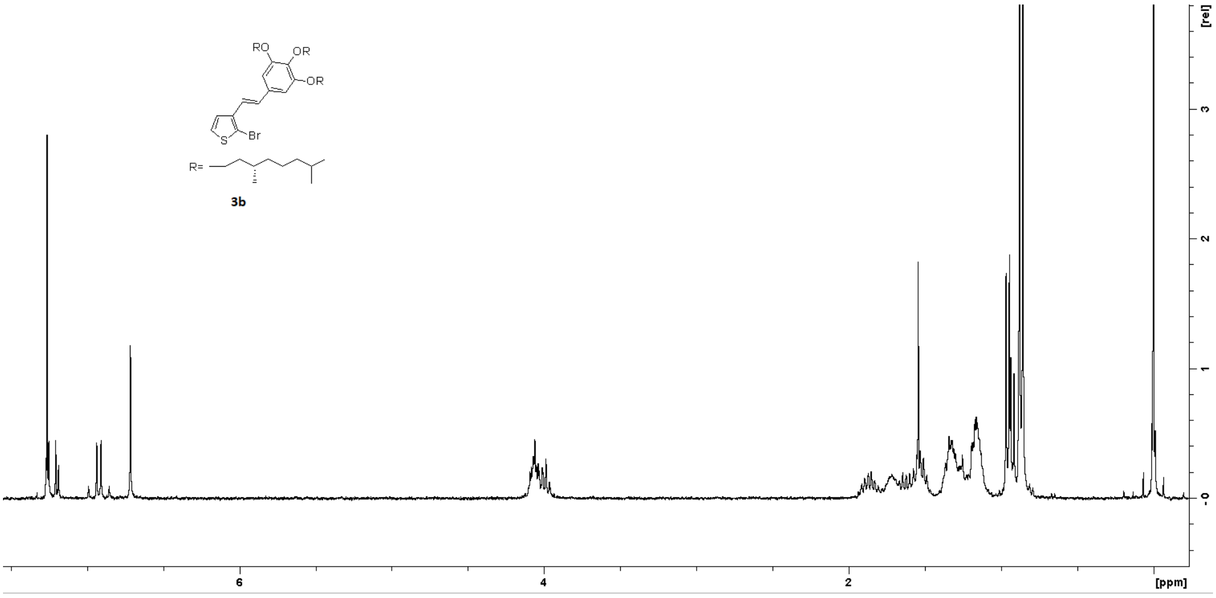

*Figure S 7. ^{1}H-NMR-spectrum of compound **3b.***

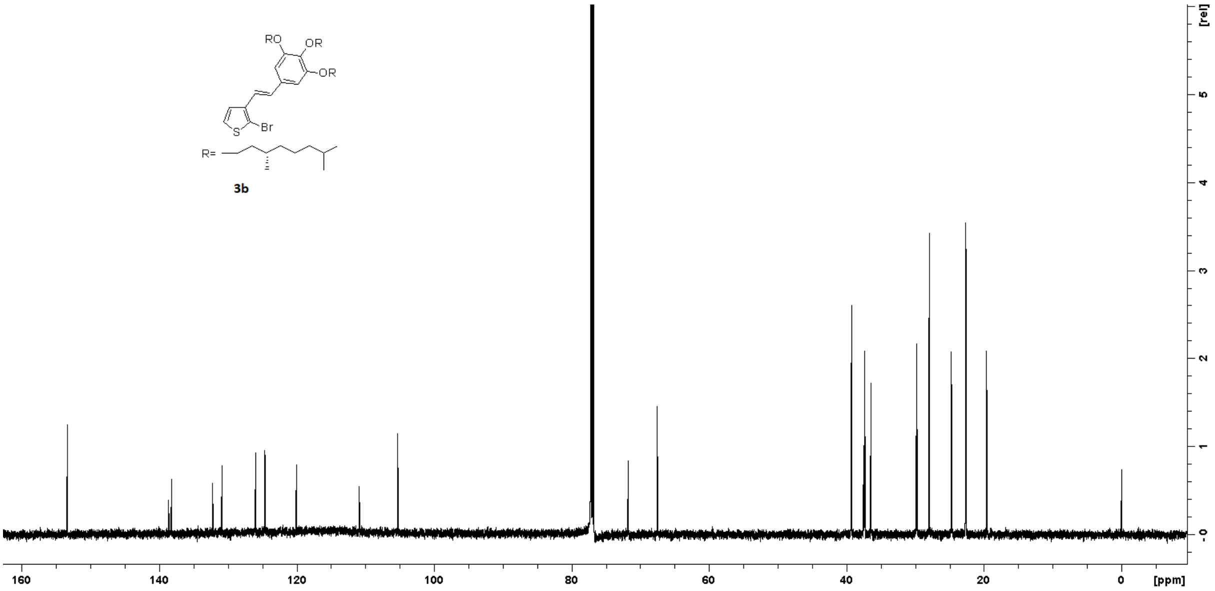

*Figure S 8. ^{13}C-NMR spectrum of compound **3b**.*

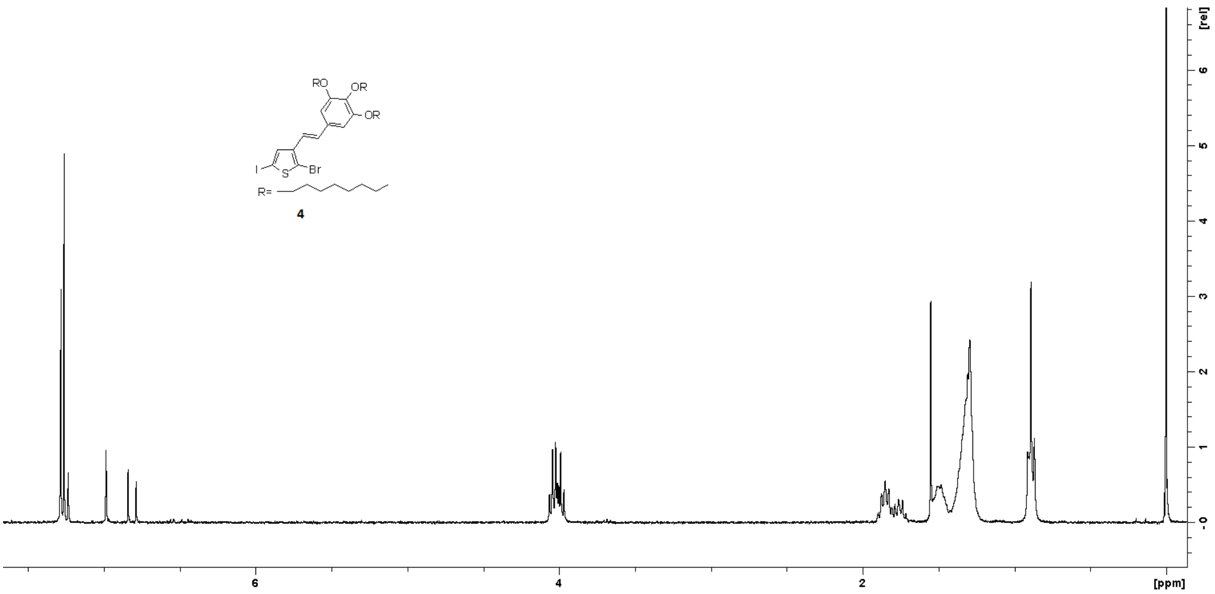

Figure S 9. *^{1}H-NMR-spectrum of compound* ***4a.***

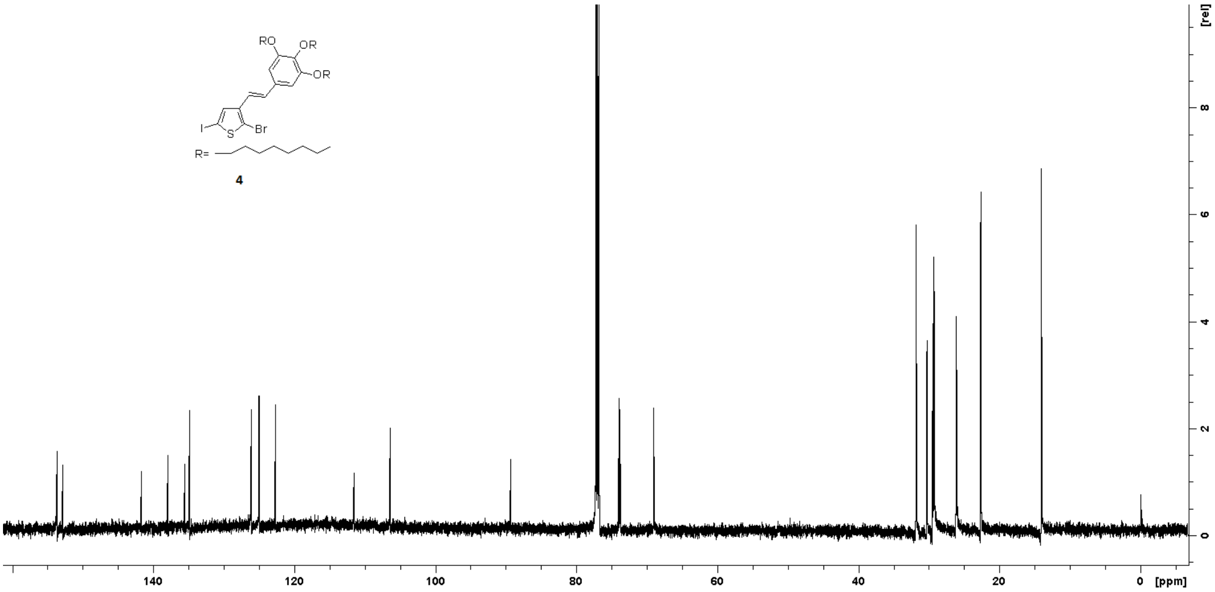

Figure S 10. *^{13}C-NMR spectrum of compound* ***4a****.*

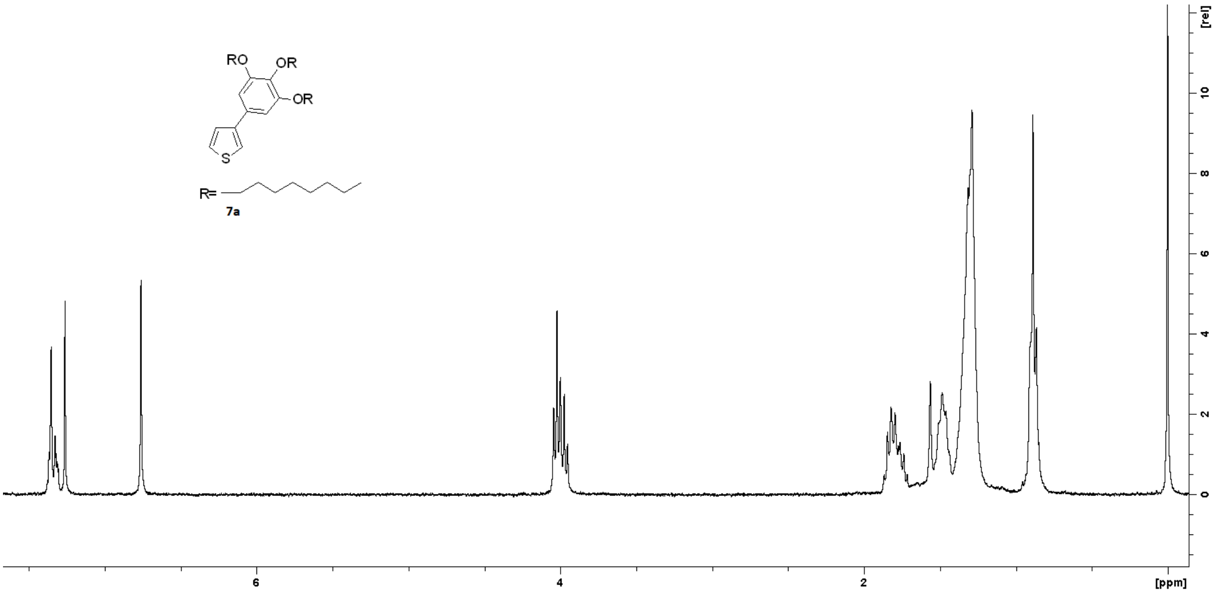

*Figure S 11. ^{1}H-NMR-spectrum of compound **7a**.*

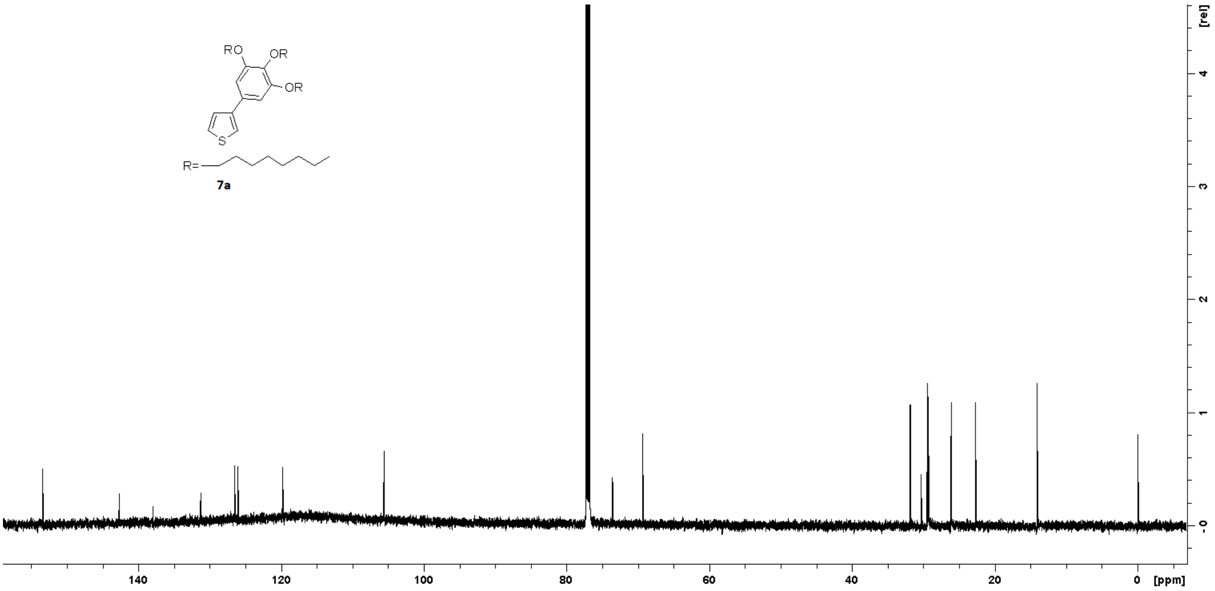

*Figure S 12. ^{13}C-NMR spectrum of compound **7a**.*

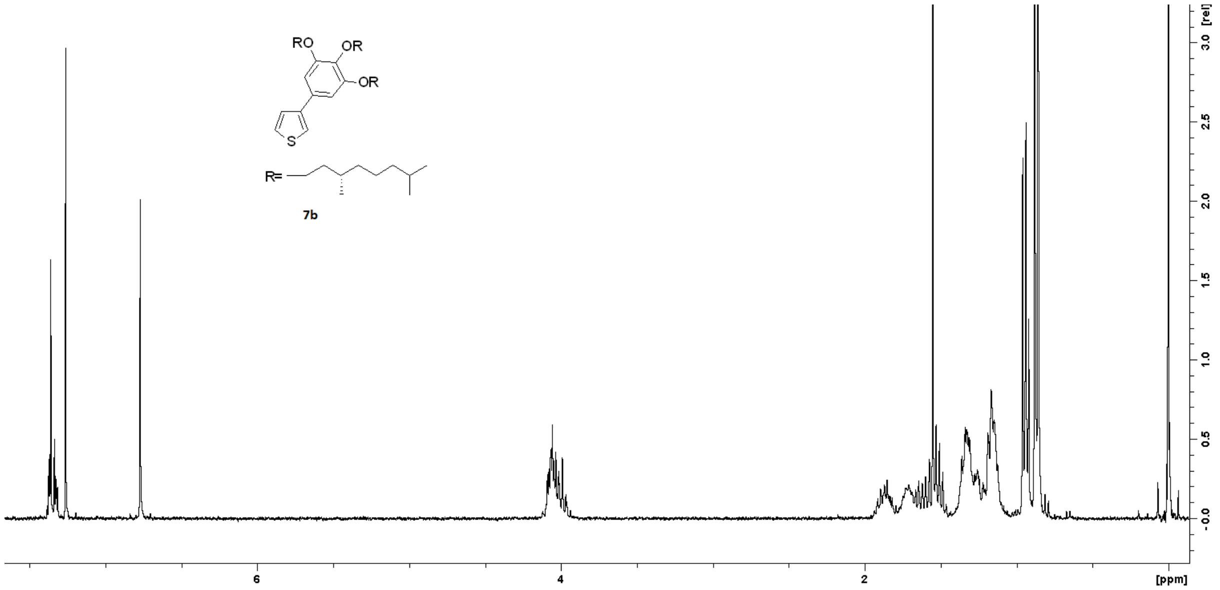

*Figure S 13. ^{1}H-NMR-spectrum of compound **7b.***

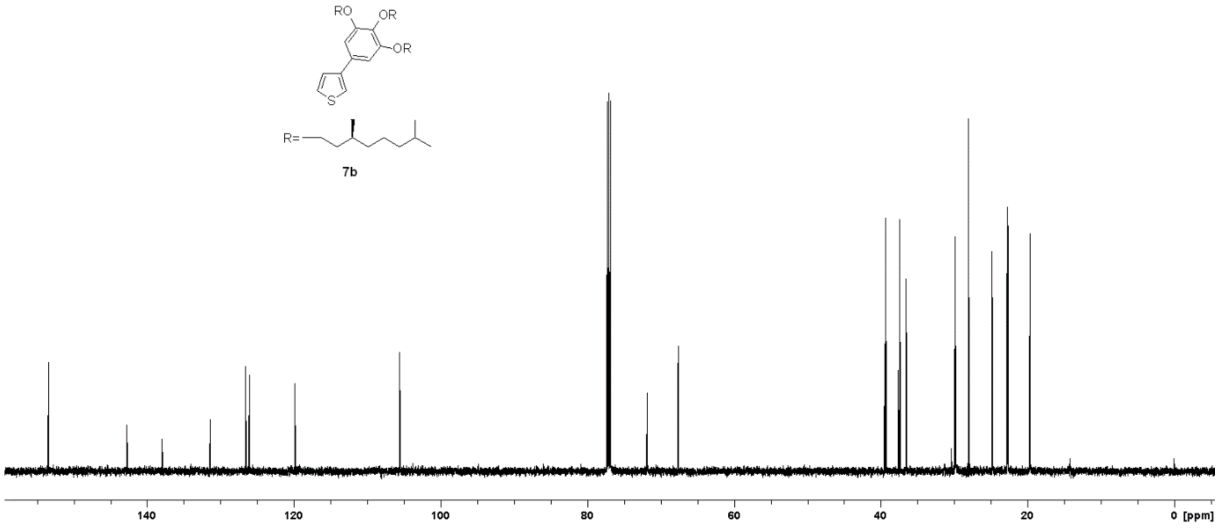

*Figure S 14. ^{13}C-NMR spectrum of compound **7b**.*

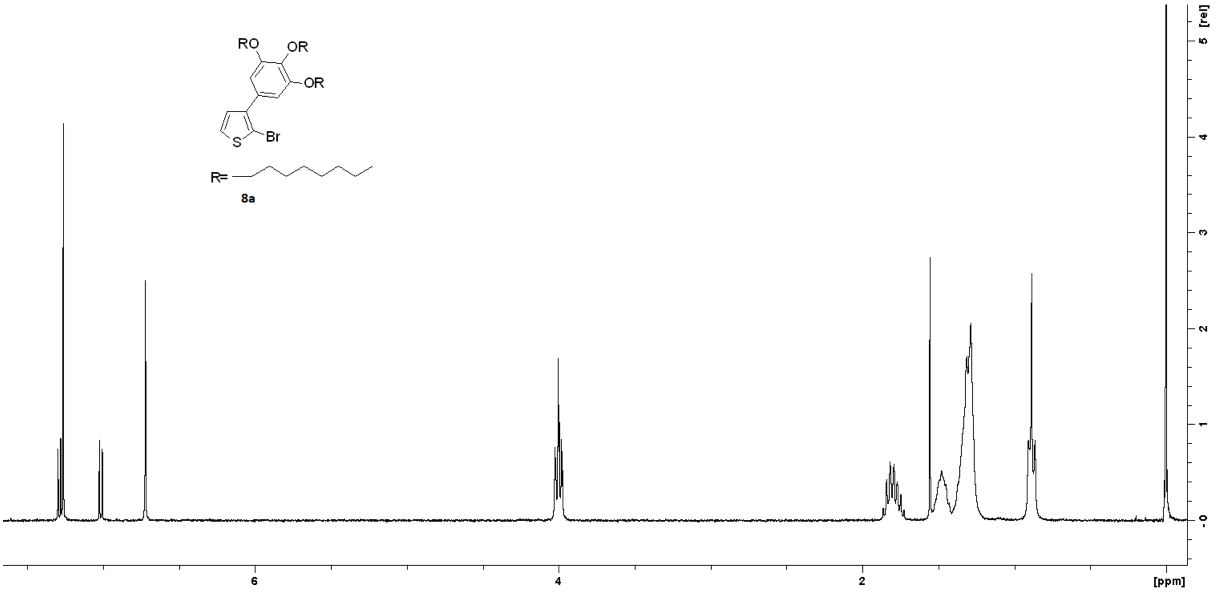

Figure S 15. ^{1}H-NMR-spectrum of compound ***8a.***

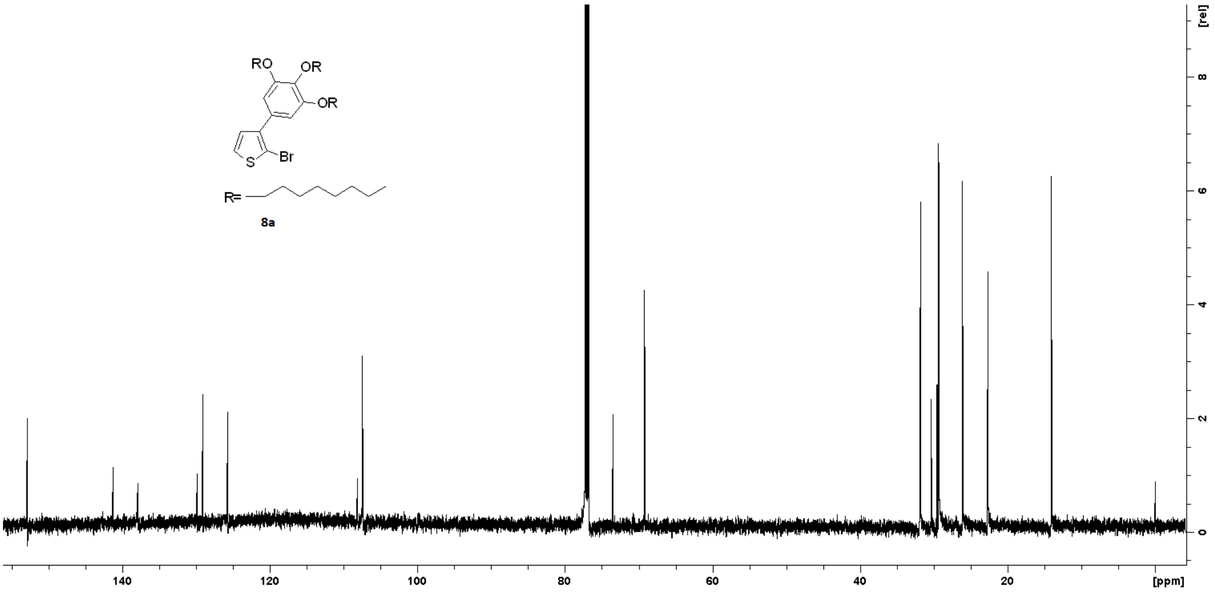

Figure S 16. ^{13}C-NMR spectrum of compound ***8a****.*

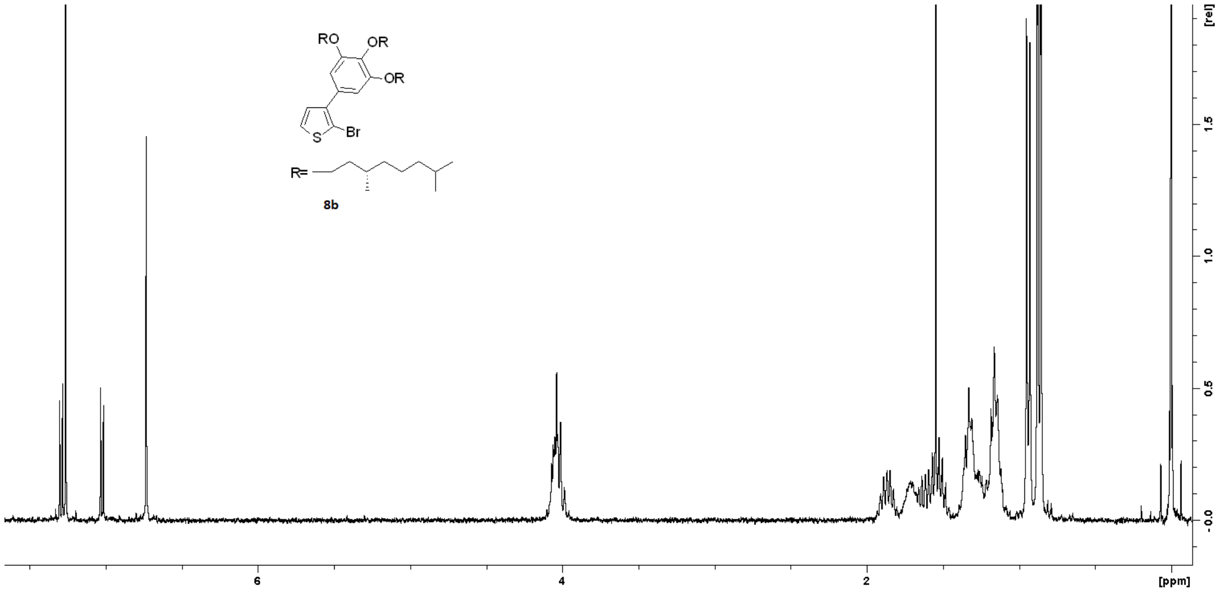

*Figure S 17. ^{1}H-NMR-spectrum of compound **8b**.*

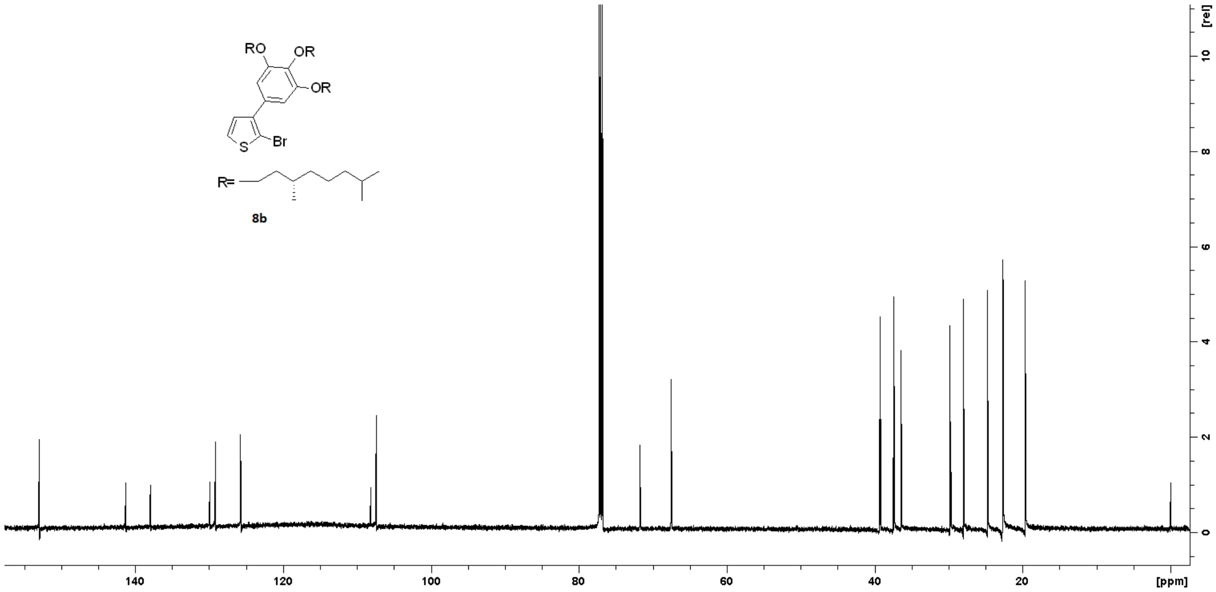

*Figure S 18. ^{13}C-NMR spectrum of compound **8b**.*

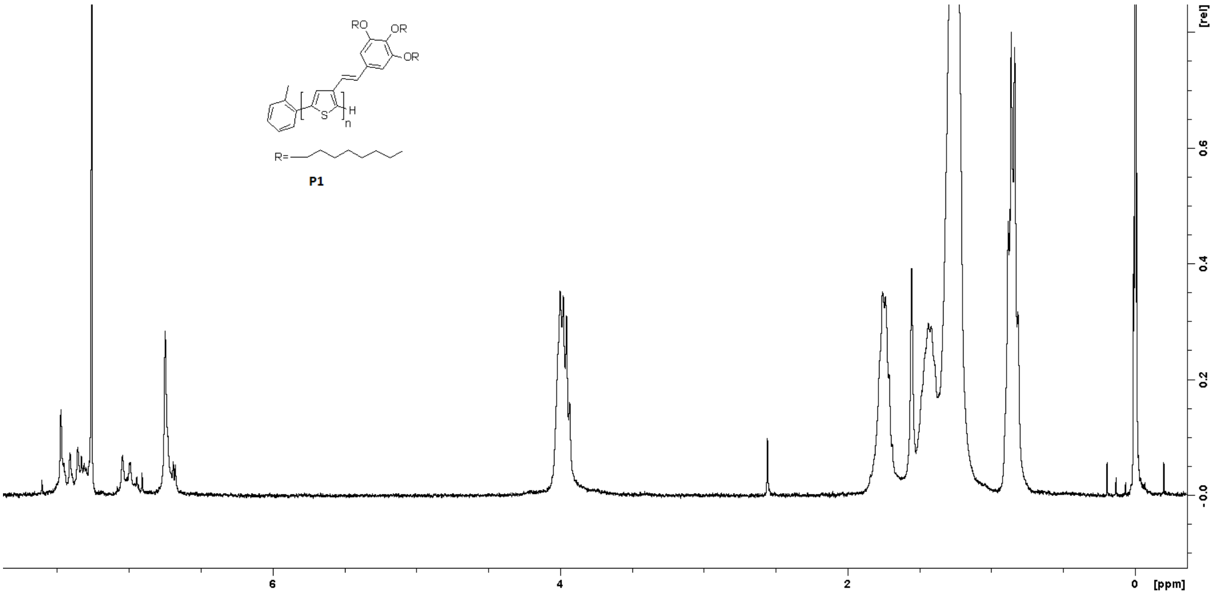

*Figure S 19. ^{1}H-NMR-spectrum of polymer **P1**.*

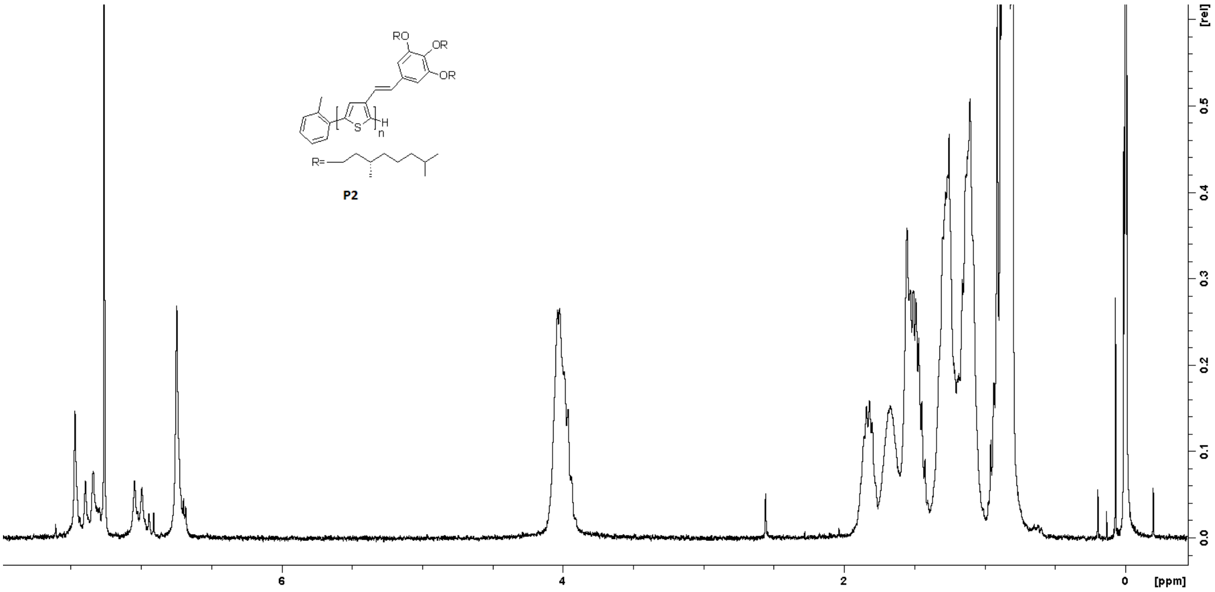

*Figure S 20. ^{1}H-NMR-spectrum of polymer **P2**.*

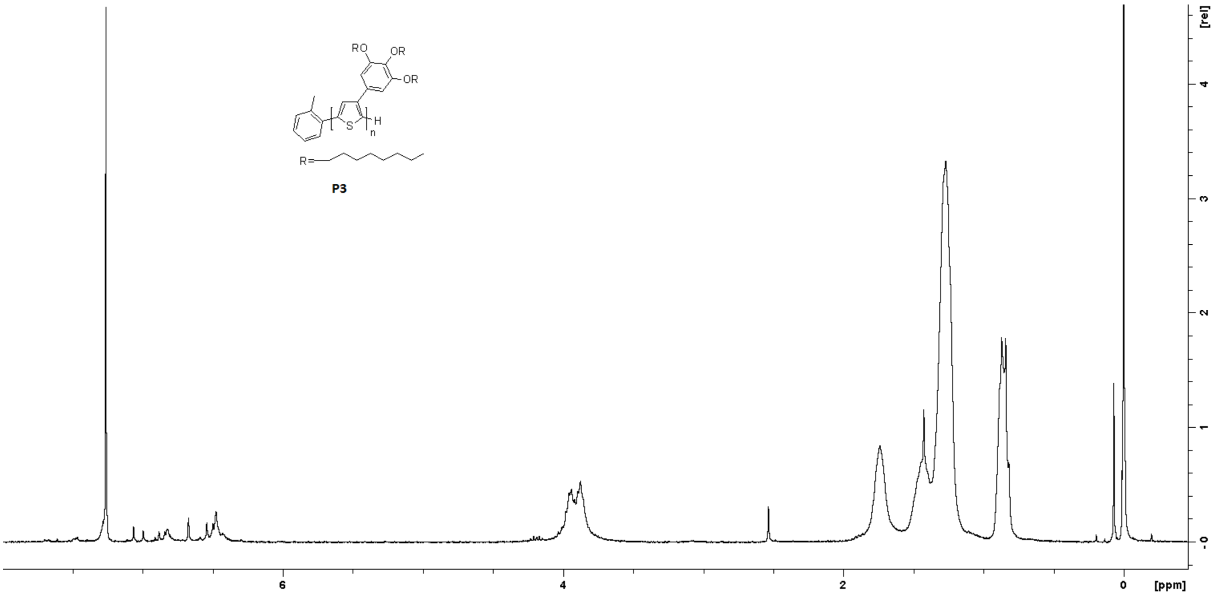

*Figure S 21. ^{1}H-NMR-spectrum of polymer **P3**.*

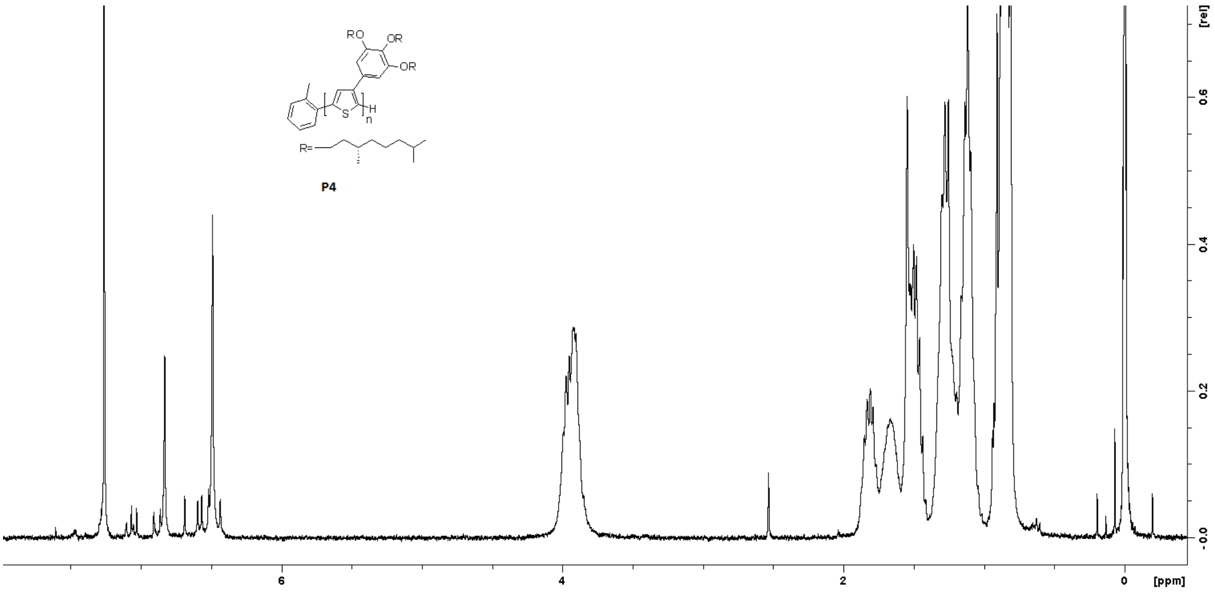

*Figure S 22. ^{1}H-NMR-spectrum of polymer **P4**.*

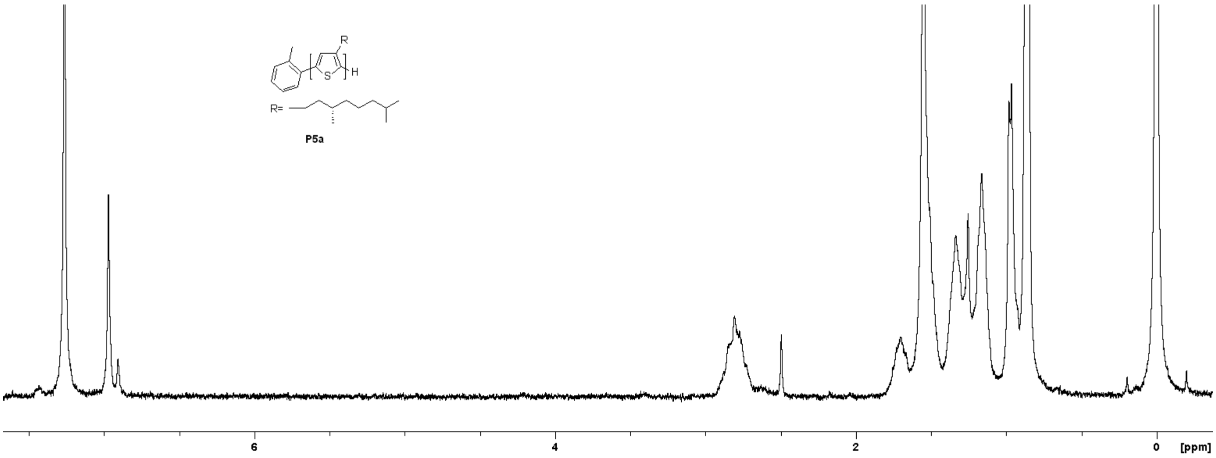

*Figure S 23. ^{1}H-NMR-spectrum of polymer **P5a**.*

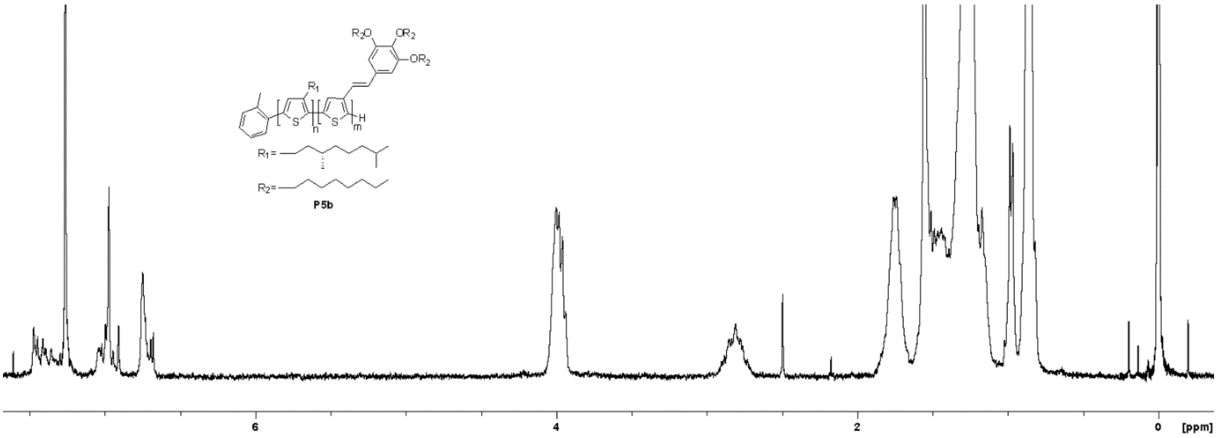

*Figure S 24. ^{1}H-NMR-spectrum of polymer **P5b**.*

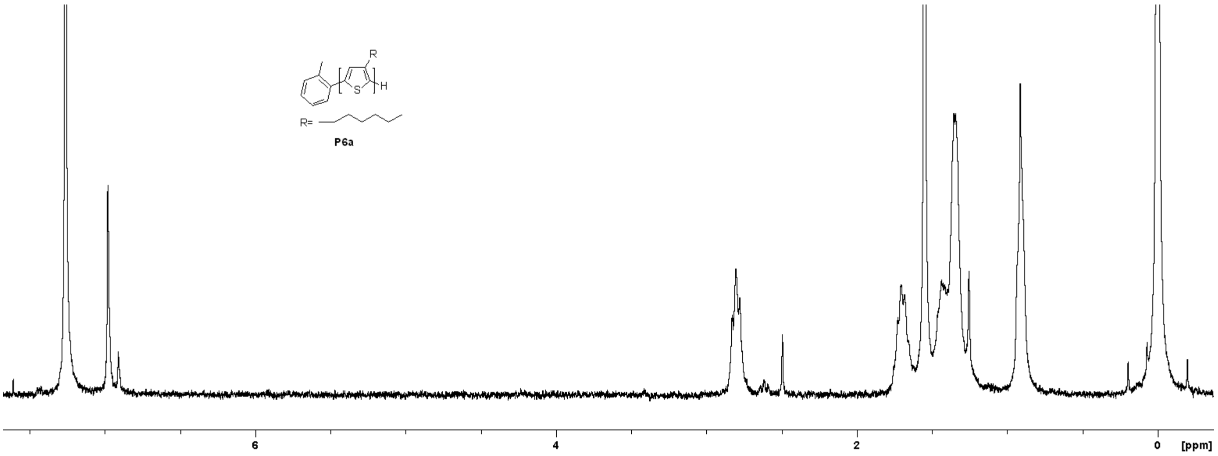

*Figure S 25. ^{1}H-NMR-spectrum of polymer **P6a**.*

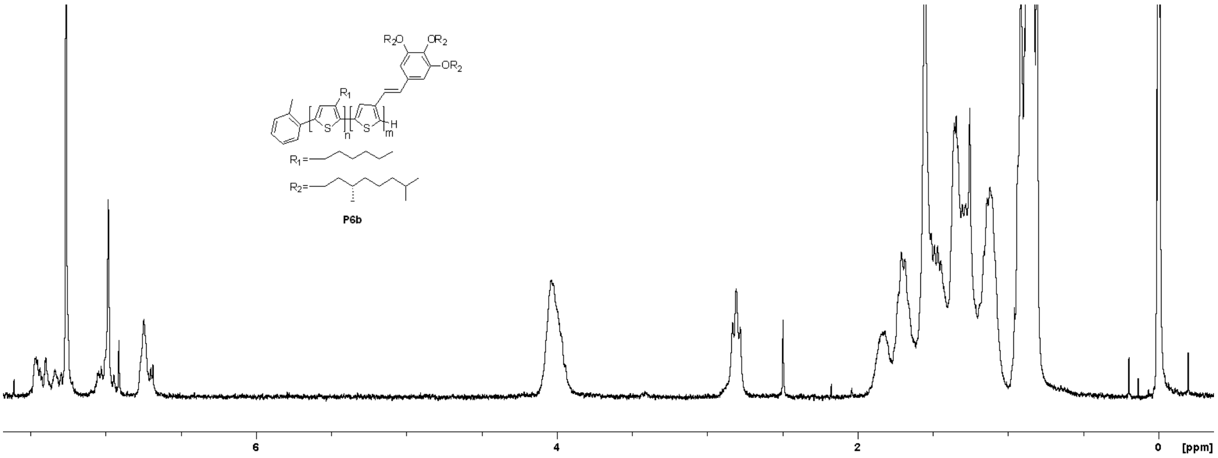

*Figure S 26. ^{1}H-NMR-spectrum of polymer **P6b**.*

Assignment of ^{1}H-NMR-spectra for determination of DP

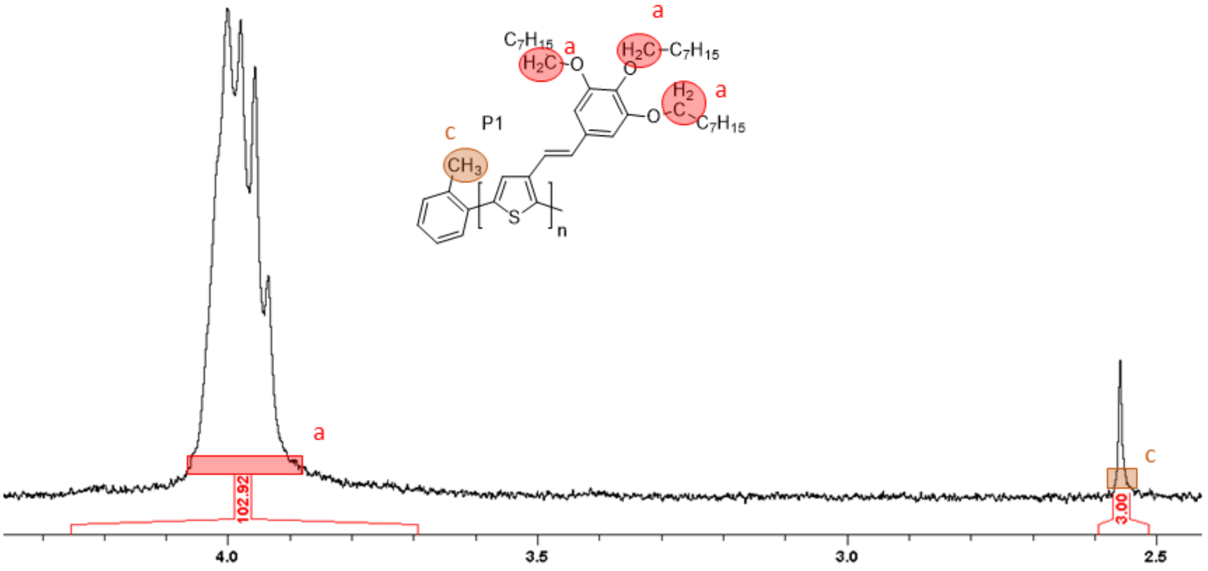

*Figure S 27. Assignment and integration of ^{1}H-NMR signals of **P1**.*

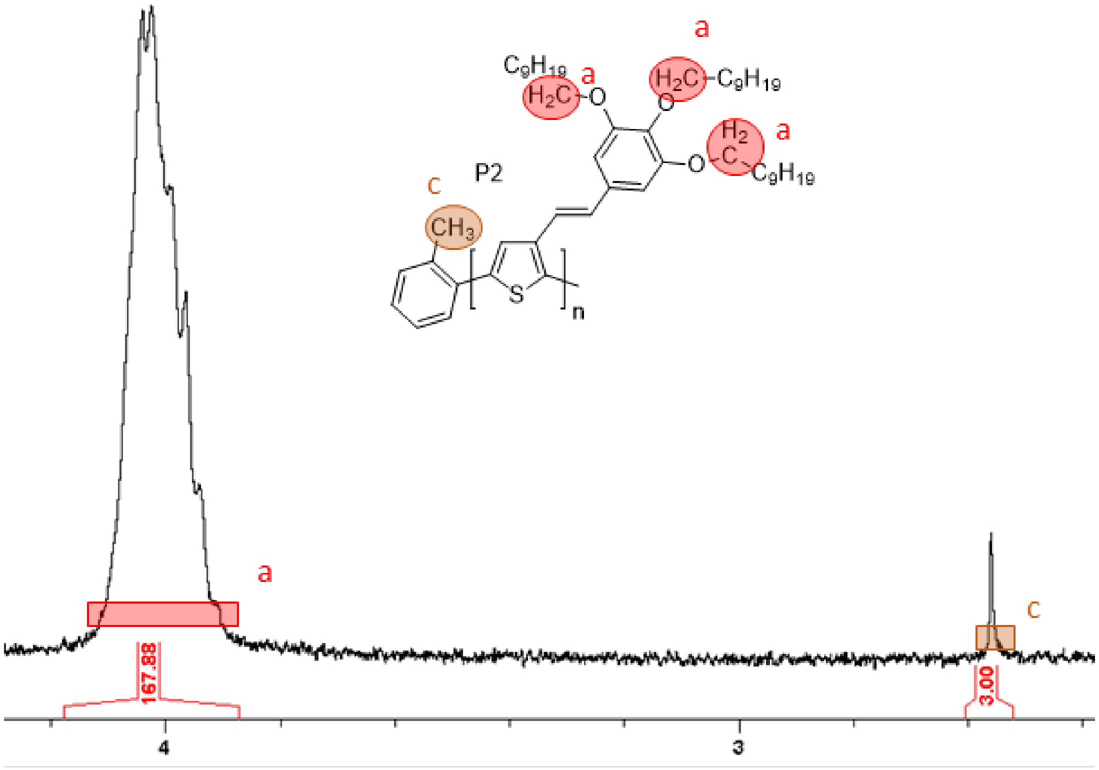

*Figure S 28. Assignment and integration of ^{1}H-NMR signals of **P2**.*

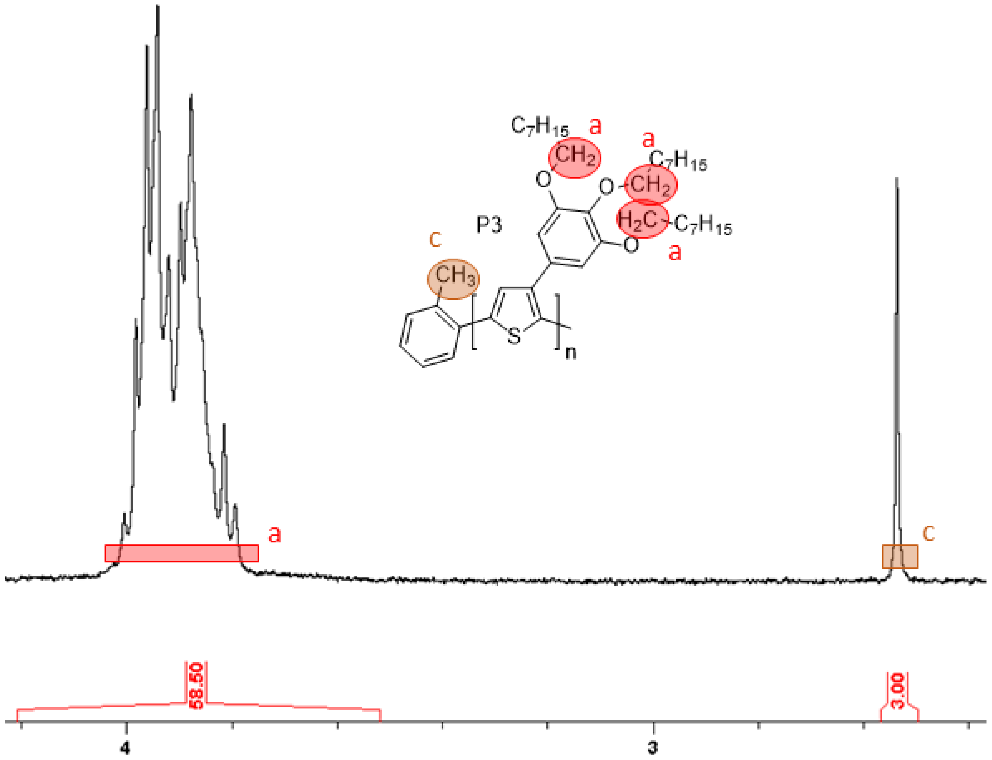

*Figure S 29. Assignment and integration of ^{1}H-NMR signals of **P3**.*

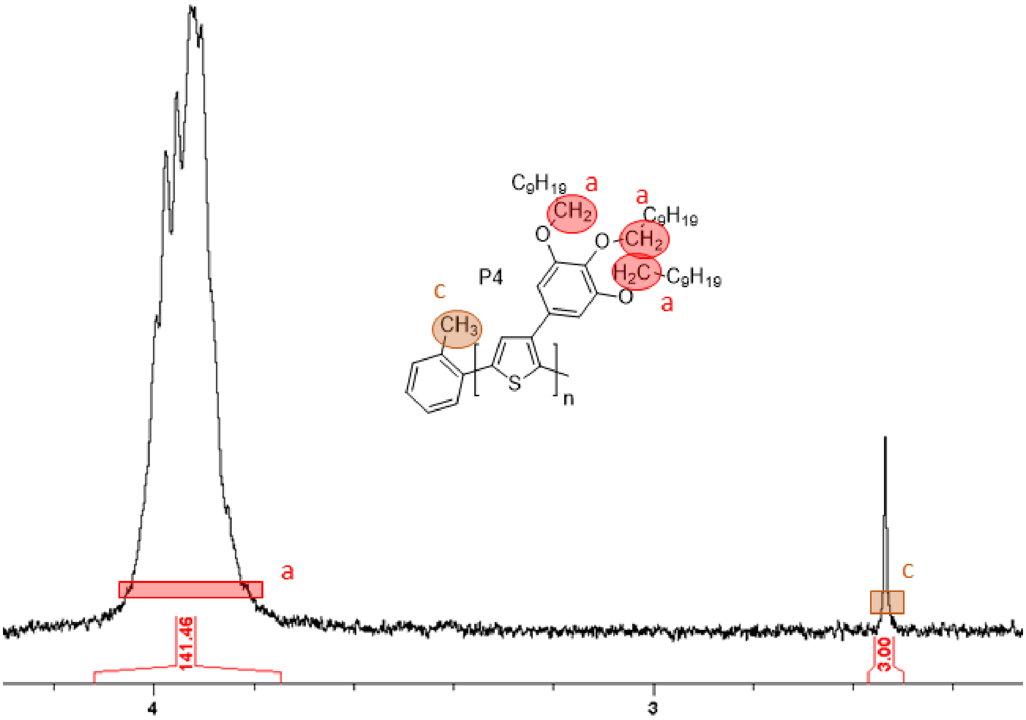

*Figure S 30. Assignment and integration of ^{1}H-NMR signals of **P4**.*

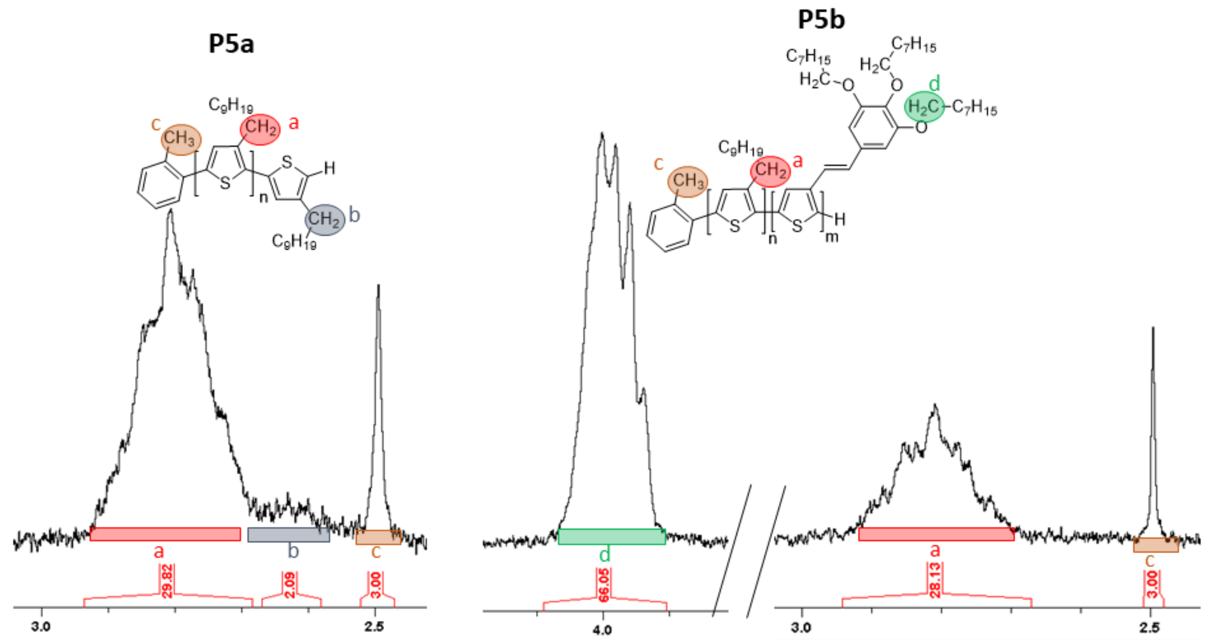

*Figure S 31. Assignment and integration of ^{1}H-NMR signals of **P5a** and **P5b**.*

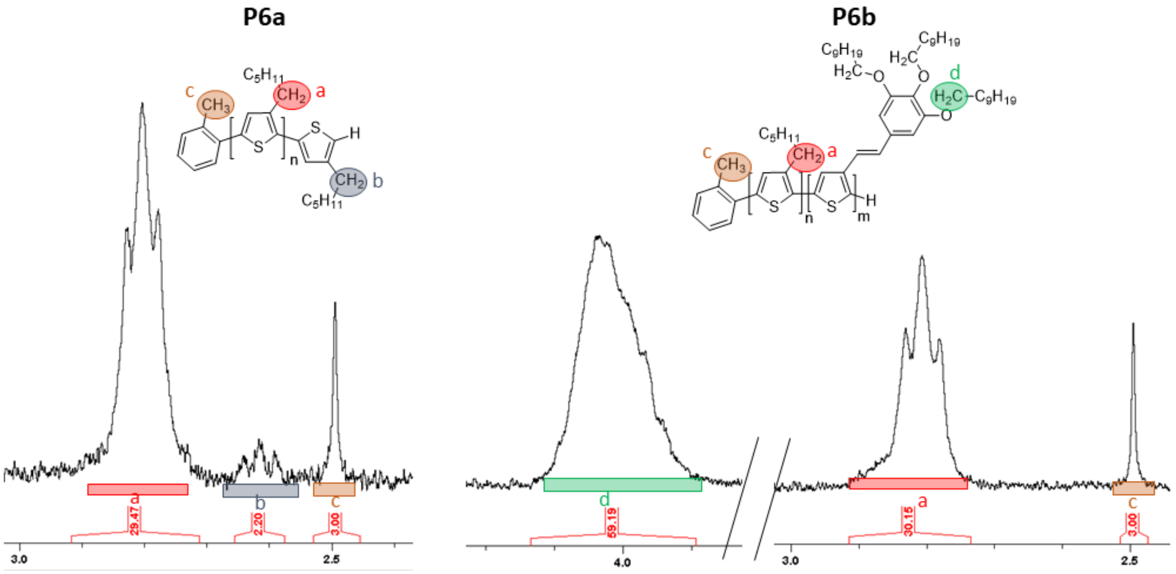

*Figure S 32. Assignment and integration of ^{1}H-NMR signals of **P6a** and **P6b***

UV-Vis spectra

The aggregation behavior of the polymers was investigated by UV-Vis. First, the polymers are dissolved in $CHCl_3$ and increasing amounts of methanol are added. A chloroform/methanol mixture in which the polymer adopts an intermediate structure is then chosen and a dilution series was made in this solvent mixture.

Polymer 1

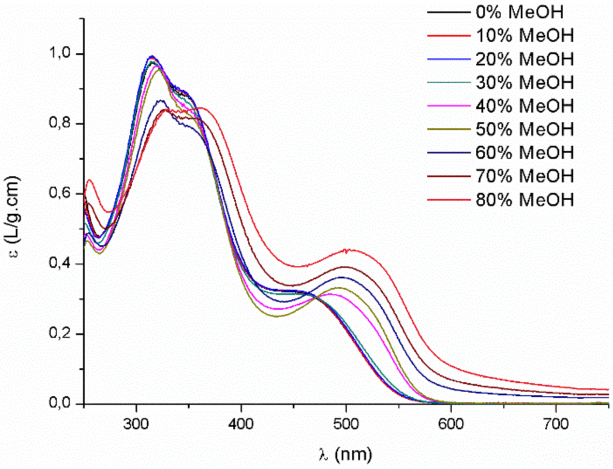

*Figure S 33 UV-Vis spectra of the solvatochroism experiment of **P1**. Concentration of all samples was 30 mg/l.*

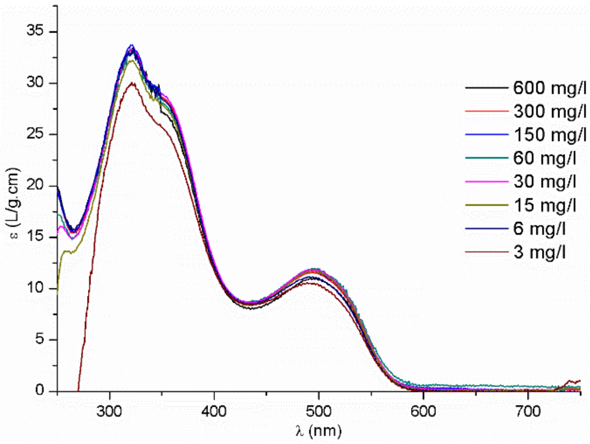

*Figure S 34. UV-Vis spectra of the dilution experiment for **P1**. Solutions were made in a $CHCl_3$/MeOH 50/50-mixture.*

Polymer 2

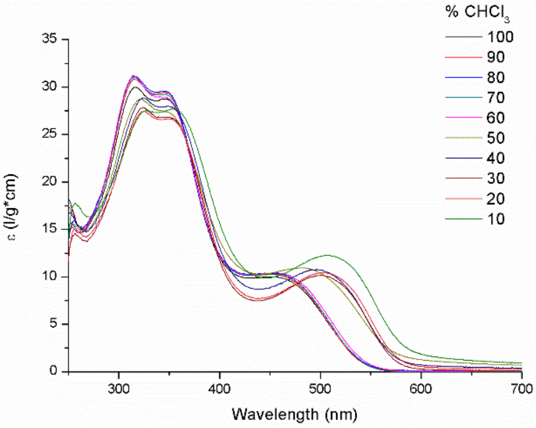

*Figure S 35. UV-Vis spectra of the solvatochroism experiment of **P2**. Concentration of all samples was 30 mg/l.*

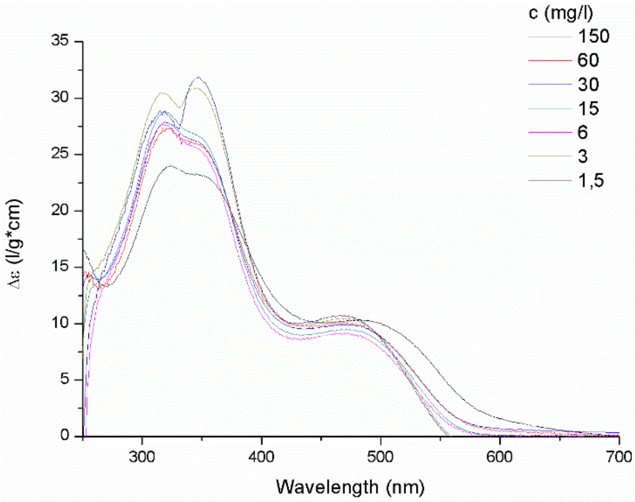

*Figure S 36. UV-Vis spectra of the dilution experiment for **P2**. Solutions were made in a $CHCl_3$/MeOH 50/50-mixture.*

Polymer 3

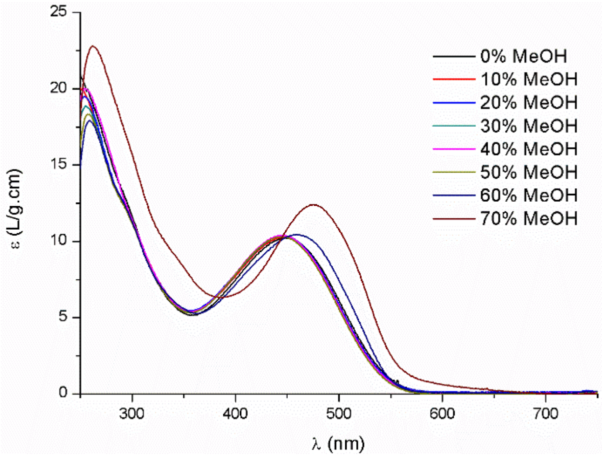

*Figure S 37. UV-Vis spectra of the solvatochroism experiment of **P3**. Concentration of all samples was 30 mg/l.*

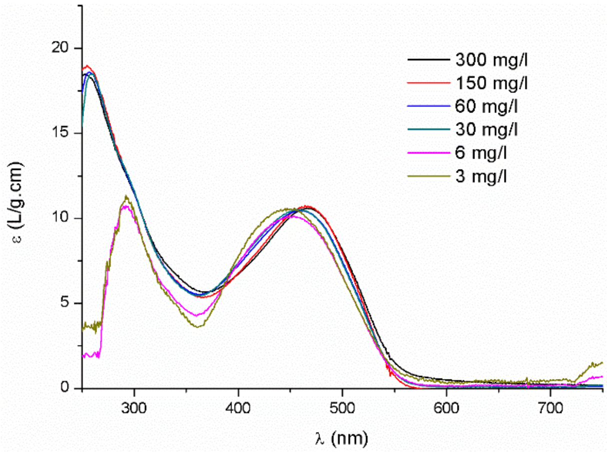

*Figure S 38. UV-Vis spectra of the dilution experiment for **P3**. Solutions were made in a $CHCl_3$/MeOH 40/60-mixture.*

Polymer 4

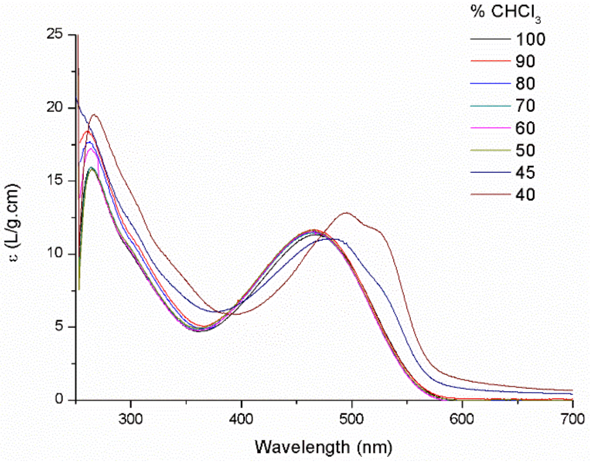

Figure S 39. UV-Vis spectra of the solvatochroism experiment of ***P4****. Concentration of all samples was 30 mg/l.*

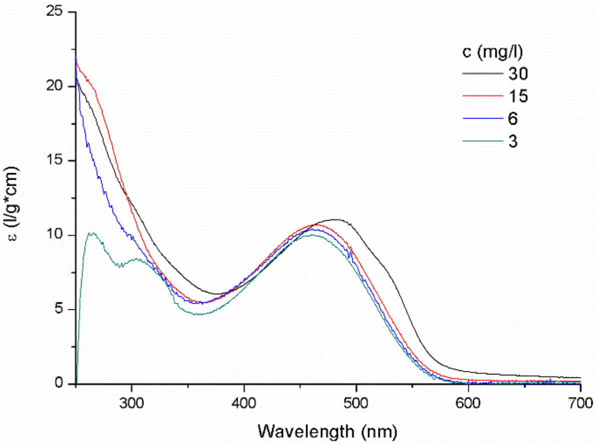

Figure S 40. UV-Vis spectra of the dilution experiment for ***P4****. Solutions were made in a CHCl$_3$/MeOH 45/55-mixture.*

Polymer 5b

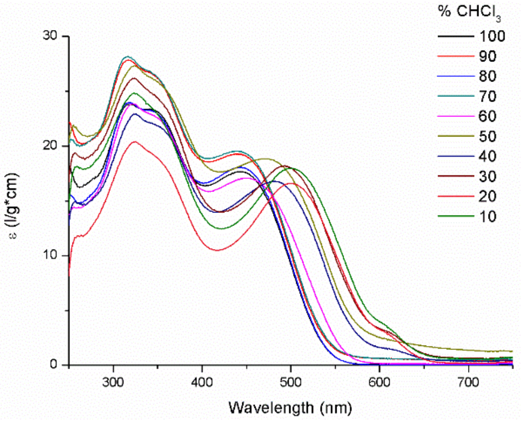

Figure S 41. UV-Vis spectra of the solvatochroism experiment of ***P5b****. Concentration of all samples was 30 mg/l.*

Polymer 6b

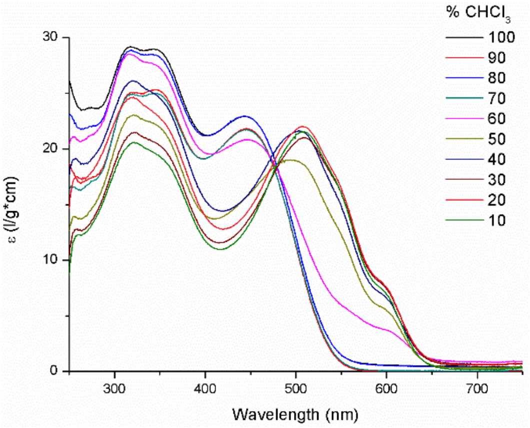

*Figure S 42. UV-Vis spectra of the solvatochroism experiment of **P6b**. Concentration of all samples was 30 mg/l.*

CD-Spectra

The aggregation behavior of the polymers was investigated by circular dichroism. First, the polymers are dissolved in $CHCl_3$ and increasing amounts of methanol are added. A chloroform/methanol mixture in which the polymer adopts an intermediate structure is then chosen and a dilution series was made in this solvent mixture.

Polymer 2

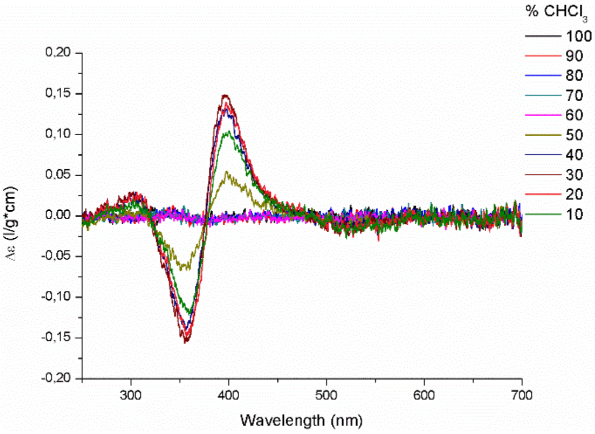

*Figure S 43. CD-spectra of the solvatochroism experiment of **P2**. Concentration of all samples was 30 mg/l.*

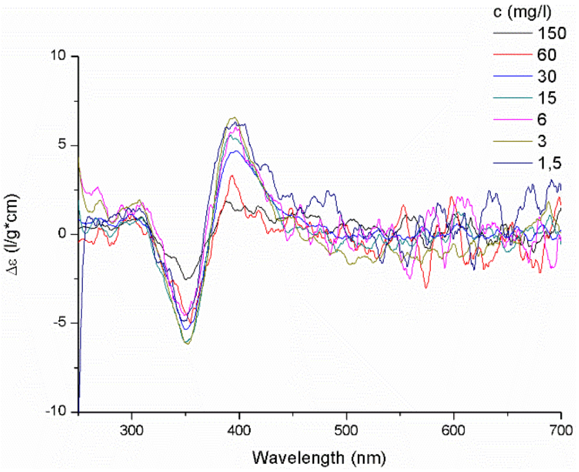

*Figure S 44. UV-Vis spectra of the dilution experiment for **P2**. Solutions were made in a $CHCl_3$/MeOH 50/50-mixture.*

Polymer 4

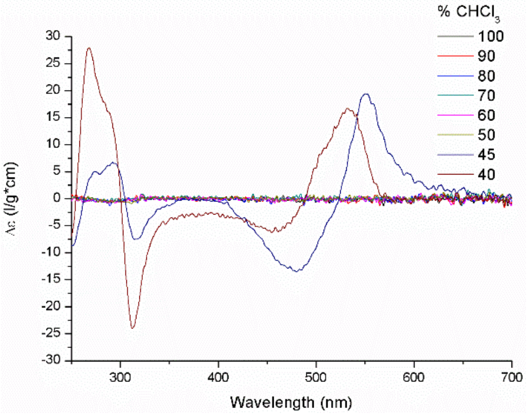

*Figure S 45. CD-spectra of the solvatochroism experiment of **P4**. Concentration of all samples was 30 mg/l.*

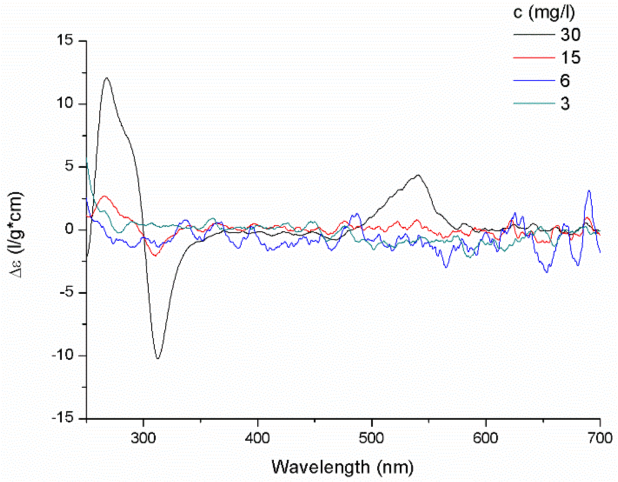

*Figure S 46. UV-Vis spectra of the dilution experiment for **P4**. Solutions were made in a $CHCl_3$/MeOH 45/55-mixture.*

Polymer 5b

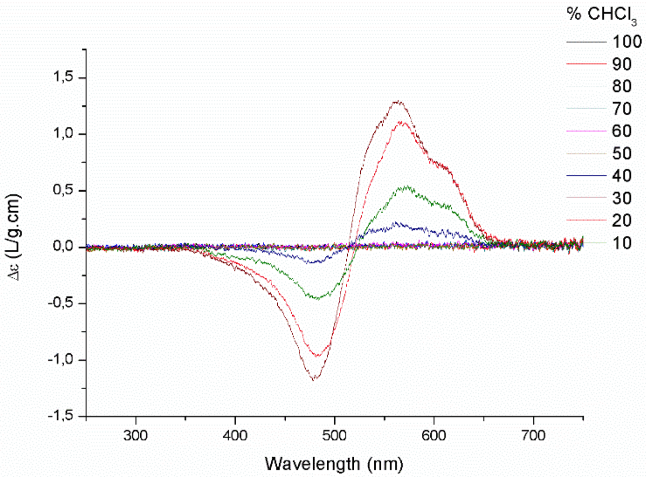

*Figure S 47. CD-spectra of the solvatochroism experiment of **P5b**. Concentration of all samples was 30 mg/l.*

Polymer 6b

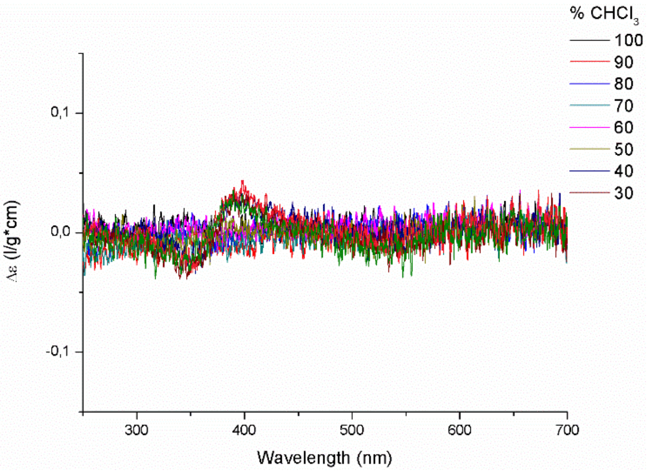

*Figure S 48. CD-spectra of the solvatochroism experiment of **P6b**. Concentration of all samples was 30 mg/l.*

GPC-Chromatograms

Variation of monomer over initiator ratio

P3PVT

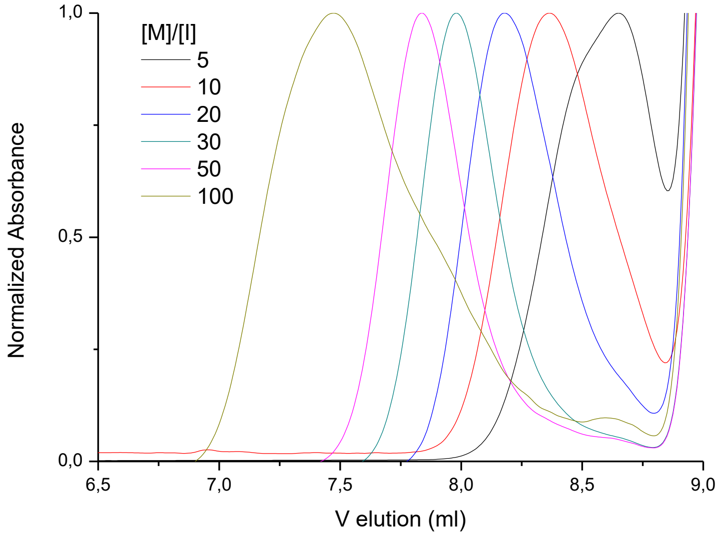

Figure S 49. GPC-traces of the monomer over initiator experiment for P3PVT. The cut-off peak at 9.5 ml belongs to the protonated monomer.

P3PT

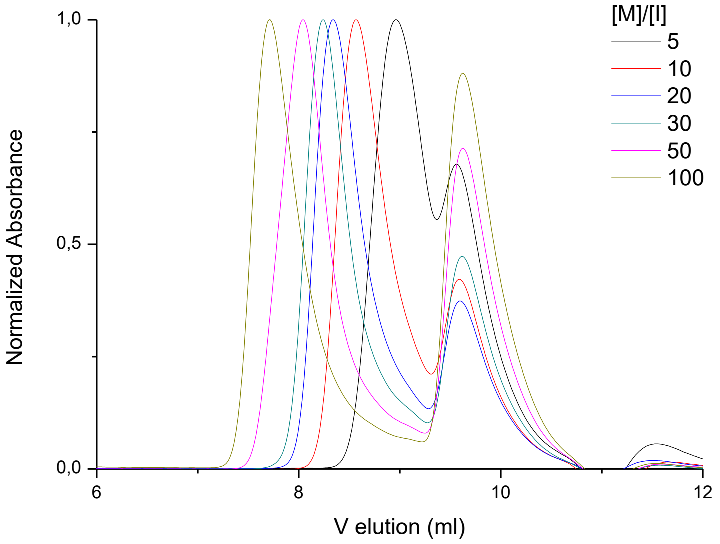

Figure S 50. GPC-traces of the monomer over initiator experiment for P3PT. The peak at 9.5 ml belongs to the protonated monomer.

Atomic force microscopy

For the experiments described in the main text, 0.2 mg.ml^{-1} solutions of **P5b** and **P6b** were prepared in toluene. Then, an equivalent volume of MeOH was added to obtain a 50/50 mixture. Solutions of the copolymers were drop-casted at room temperature within 1h after addition of MeOH (the polymers tend to precipitate after some time) on a freshly cleaved highly oriented pyrolytic graphite sample (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA). Deposition occurred in saturated atmosphere to allow solvent to evaporate overnight in order to let the system approach thermodynamic conditions. In the case of pure toluene solutions, similar drop-casting was performed with 0.1 mg.ml^{-1} solutions of **P5b** and **P6b**. AFM measurements were carried out in air using a PicoSPM (Agilent) instrument in intermittent contact mode. Olympus silicon cantilevers (OMCL-AC160TS and AC240TS) were used. AFM images were processed using WSxM (Nanotec Electronica, Spain).[8]

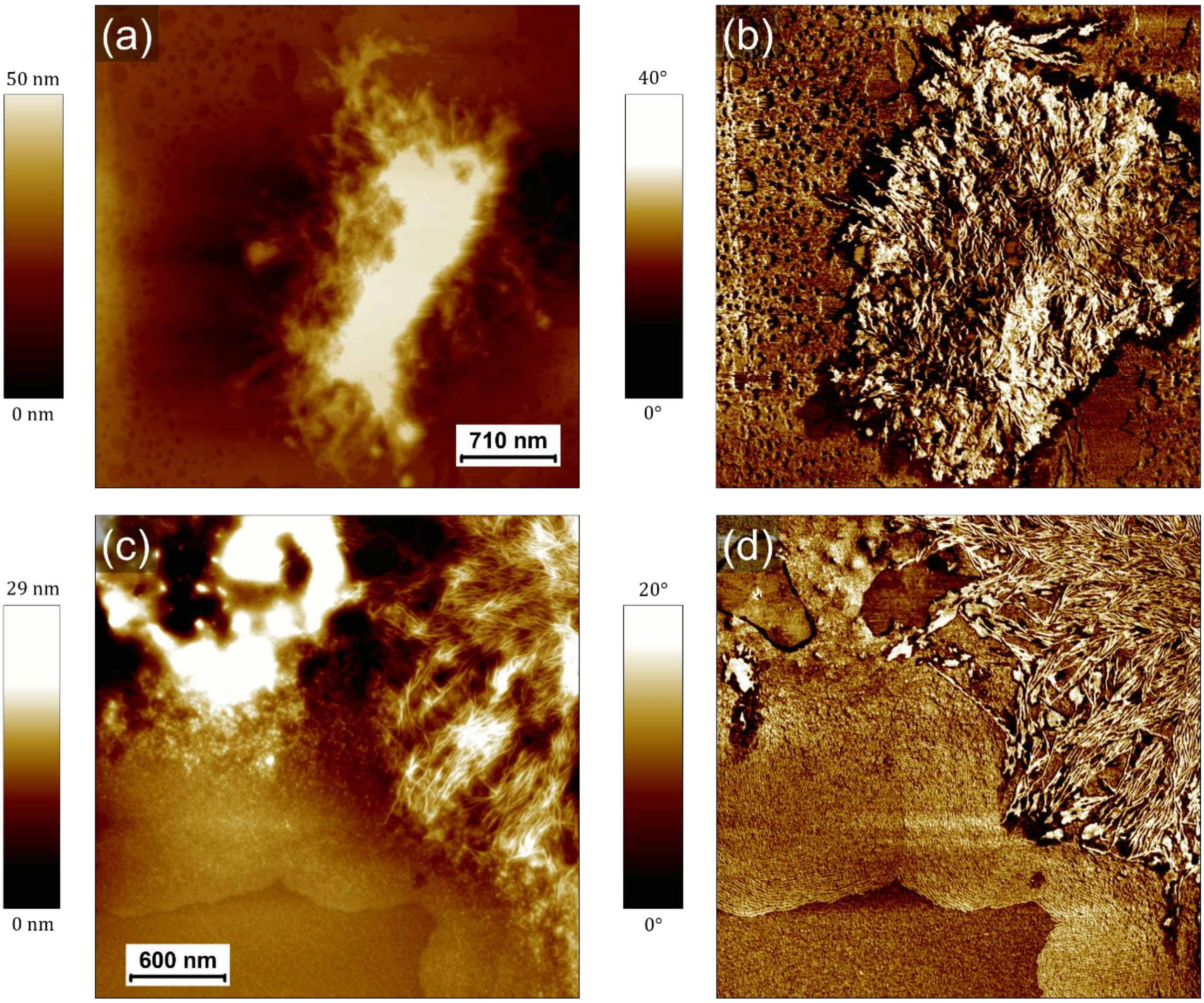

Figure S 51

Large-scale AFM images of dry polymer films drop-casted on graphite. (a) Topography and (b) corresponding phase image of **P5b**; (c) topography and (d) corresponding phase image of

P6b. AFM images presented in the main text correspond to high resolution images obtained in the regions shown here, where mono- and multi-layers coexist.

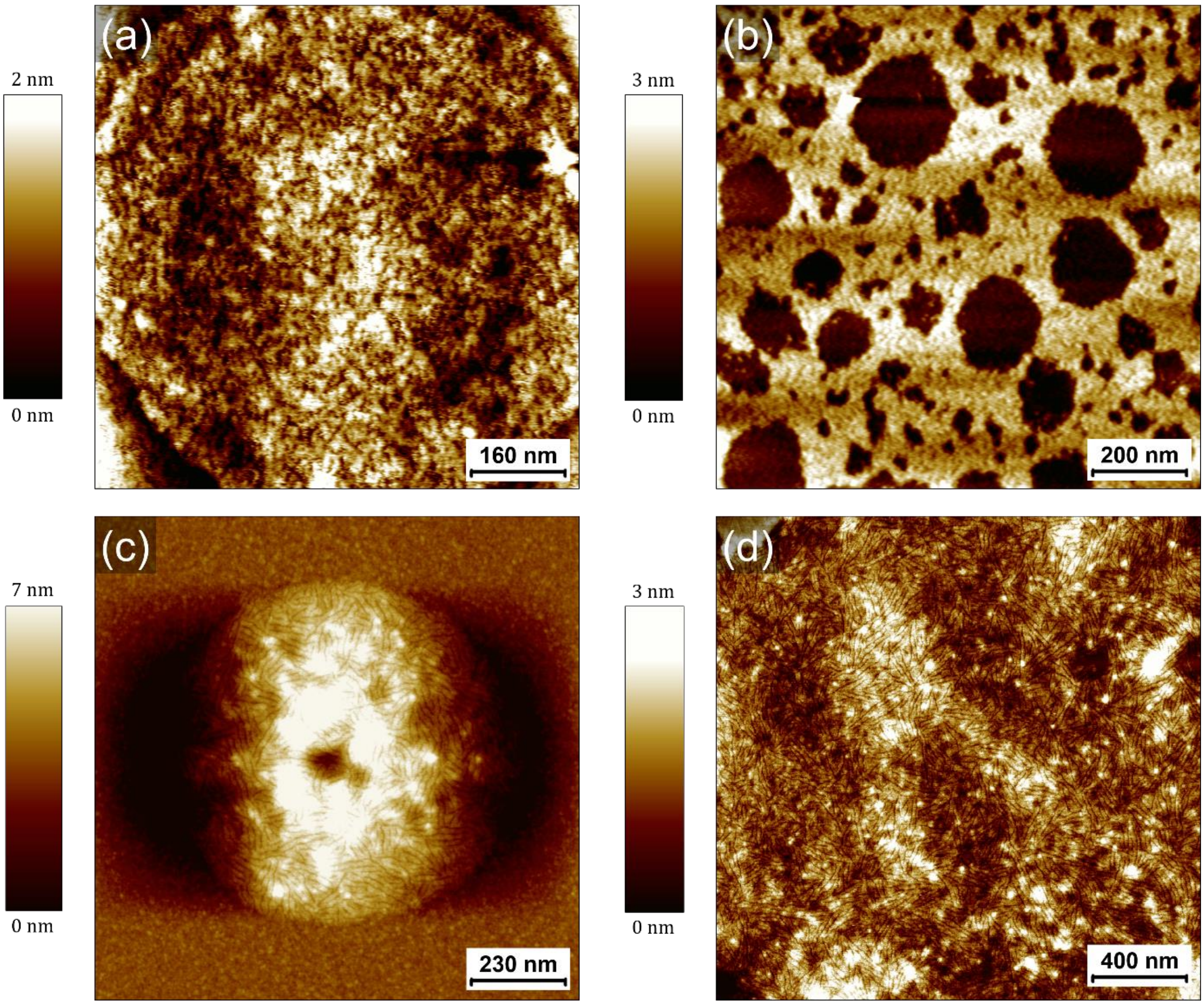

Figure S 52. AFM topography images of **P5b** (a, b) and **P6b** (c, d) obtained by drop-casting of 0.1 mg.ml^{-1} solutions in toluene. While **P5b** did not show any organized structure, **P6b** exhibits fibers in some regions, that can be in the form of small spherical assemblies (c) or more uniform layers (d). Those fibers have the same width as those shown in the main text, but are much smaller in length, suggesting that the addition of a non-solvent improves the assembly.

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