Conformational Behavior of Conjugated Polymers With Oligo(phenylene vinylene) Side chains

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In this paper the synthesis and chiroptical properties of a series of *meta*-arylenes, equipped with chiral oligo(phenylene vinylene)s (OPVs) side-chains, is presented. It is investigated how the OPV side-chain contributes to the optical properties of the polymer. Second, the influence of the distance of the chiral moieties, placed on the OPV side-chain, to the polymer main chain is investigated, which showed that in order to induce any chiral effects, these chiral moieties need to be placed in β -position near the polymer main chain. Finally, it was shown that long (a)chiral, lateral alkoxy chains on the OPV side-chain prevent the polymers to adopt a helical conformation and results in the formation of lateral (a)chiral stacks of different polymer chains.

Introduction

As bare CPs are insoluble materials, substituents - typical aliphatic groups - are introduced. These substituents indeed render the material soluble and processable. Moreover, they can promote and stabilize a particular supramolecular or macromolecular structure and as such contribute to the promising properties of these materials. For instance, the alkyl group in poly(3-alkylthiophene)s favors a lamellar structure, which is beneficial for oLEDs and solar cells.^[1-3] A gallic acid moiety, on its turn, can promote the formation of a helical structure.^[4-7] Finally, the substituent can also be used to introduce chirality in the polymer. If, however, CPs are equipped with a conjugated rather than an aliphatic side-chain, the substituent does

not only introduce solubility and possibly chirality in the materials, but it can also contribute to its optical and electronic properties.^[8–17]

In this manuscript, CPs with a general structure as proposed in **Figure 1** are studied. The polymers are composed of an aryl group (a bithiophene or thienothiophene) coupled with a *meta*-phenylene group. A *meta*-phenylene linkage was chosen, since it might aid in the formation of a helical structure, as found in poly(*meta*-phenylene acetylene)s,^[18,19] and since it allows the introduction of the substituent preserving a symmetric structure. (Chiral) alkyl groups are introduced for solubility and chirality reasons. It will be investigated (i) whether the OPV side-chain indeed contributes to the optical properties of the CP, (ii) how the molecular structure of the OPV side-chain determines whether the polymer folds into a helix or that it stacks in a poor solvent, and (iii) how the molecular structure of the OPV side-chain determines whether chirality is expressed.

Experimental Section

All reagents were purchased from Sigma Aldrich, Acros Organics, Merck and Alfa Aesar. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). Gel Permeation Chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran as eluent toward polystyrene standards. Mass spectra were recorded using an Agilent HP5989. ¹H nuclear magnetic resonance (¹H NMR) measurements were carried out with a Bruker Avance 300 MHz. UV-vis measurements were performed on a Perkin Elmer Lambda 900 UV-vis NIR. The DSC spectra were recorded on a Perkin Elmer DSC 7.

Compounds **1**,^[20] **2**,^[21] **3**,^[22] **4**,^[23] **11**,^[24] **13**^[25] and **16**^[26] were prepared as described in literature.

Monomer Synthesis

Synthesis of (*E*)-2,5-di(decyloxy)-4-(3,5-dibromostyryl)benzaldehyde (**6**)

K^t-BuO (1.50 mmol; 168 mg) was added to a solution of **2** (1.50 mmol; 579 mg) in THF (1M) at room temperature and under an argon atmosphere. After 5 min, **1** (1.50 mmol; 667 mg), dissolved in THF (1M), was added to the reaction mixture and the mixture was stirred for another 4h. After reaction, a saturated NH₄Cl-solution was added and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with a saturated NaCl-solution, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was dissolved in THF and precipitated in MeOH resulting in a yellow solid (319 mg, yield = 31%).

mp 53-54°C; ¹H NMR (300 MHz, CDCl₃, δ): 10.45 (s, H, CHO), 7.59-7.56 (s (br), 3H, Ar H), 7.42 (d (*J*= 16.2 Hz), 1H, CH), 7.34 (s, 1H, Ar H), 7.11 (d (*J*= 16.2 Hz), 1H, CH), 7.11 (s, 1H, Ar H), 4.06 (m, 4H, CH₂), 1.90-1.81 (m, 4H, CH₂), 1.51-1.23 (m, 24H, CH₂), 0.88 (m, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 189.0, 156.0, 151.0, 141.0, 133.1, 132.9, 129.3, 128.4, 126.0, 124.9, 123.3, 111.3, 110.3, 69.3, 69.2, 31.9, 29.7, 29.6, 29.4, 29.4, 29.3, 29.3, 29.2, 26.3, 26.1, 22.7, 14.1; CIMS *m/z*: 678 [M⁺].

Synthesis of diethyl-2,5-di(decyloxy)-4-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)styryl]benzylphosphonate (**7**)

The same procedure was followed as described for the synthesis of **6**, starting from K^t-BuO (500 μmol; 56.1 mg), **4** (500 μmol; 338 mg) and **3** (500 μmol; 288 mg). The crude product was further purified by column chromatography (silica gel; eluent: EtOAc/*n*-hexane (4/6)) to give a pale yellow viscous oil (1.30 g, yield = 79%).

[α]_D²⁰ = +11.0 deg·dm⁻¹·g⁻¹·mL (*c* = 1.1 g/100 ml in THF); ¹H NMR (300 MHz, CDCl₃, δ): 7.31 (d (*J*= 16.1 Hz), 1H, CH), 7.03 (s, 1H, Ar H), 6.98 (d (*J*= 16.1 Hz), 1H, CH), 6.95 (d (*J*= 2.6 Hz), 1H, Ar H), 6.72 (s, 2H, Ar H), 4.09-3.96 (m, 4H, CH₂), 3.24 (d (*J*= 21.8 Hz), 2H, CH₂), 1.94-1.42 (m, 20H, CH₂, CH), 1.39-1.11 (m, 48H, CH₂), 0.96-0.85 (m, 33H, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 153.3, 151.0, 150.4, 138.2, 133.2, 128.8, 126.0, 122.8, 120.5, 116.0, 109.6, 105.1, 71.9, 69.4, 69.0, 67.4, 61.9, 39.4, 39.3, 37.6, 37.4, 37.3, 36.5, 31.9, 29.9,

29.7, 29.7, 29.6, 29.5, 29.4, 28.0, 26.3, 24.7, 22.7, 22.7, 22.6, 19.6, 16.4, 16.3, 14.1; APCIMS m/z : 1111 [M^+].

Synthesis of 5-[4-[4-(3,5-dibromostyryl)-2,5-di(octyloxy)styryl]-2,5-di(octyloxy)styryl]-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene (**8**)

The same procedure was followed as described for the synthesis of **6**, starting from *Kt*-BuO (233 μ mol; 63.6 mg), **6** (233 μ mol; 158 mg) and **7** (233 μ mol; 259 mg). The crude product was dissolved in THF and precipitated in MeOH resulting in a yellow solid (336 mg, yield = 88%).

mp 93-95°C; $[\alpha]_D^{20} = +3.75 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL}$ ($c = 1.9 \text{ g}/100 \text{ ml}$ in THF); ^1H NMR (300 MHz, CDCl_3 , δ): 7.57 (s (br), 2H, Ar H), 7.51 (s, 1H, Ar H), 7.48 (s, 1H, Ar H), 7.43 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.34 (d ($J = 16.2 \text{ Hz}$), 1H, CH), 7.16 (s, 1H, Ar H), 7.15 (s, 1H, Ar H), 7.10 (s, 1H, Ar H), 7.05 (s, 1H, Ar H), 7.03 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.00 (d ($J = 16.2 \text{ Hz}$), 1H, CH), 6.74 (s, 2H, Ar H), 4.10-3.98 (m, 14H, CH_2), 1.91-1.45 (28H, CH_2 , CH), 1.39-1.16 (m, 66H, CH_2), 0.97-0.92 (m, 9H, CH_3), 0.89-0.85 (m, 30H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , δ): 153.3, 151.5, 151.2, 151.0, 151.0, 141.9, 138.3, 133.3, 132.3, 129.0, 128.7, 128.0, 127.3, 127.1, 126.7, 125.7, 125.4, 124.1, 123.2, 123.1, 122.7, 111.2, 110.8, 110.6, 110.4, 105.3, 71.8, 69.6, 69.5, 69.5, 69.4, 67.5, 39.4, 39.3, 37.6, 37.5, 37.4, 36.5, 31.9, 29.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 28.0, 26.5, 26.4, 26.3, 26.3, 24.8, 22.7, 22.6, 19.6, 14.1; APCIMS m/z : 1636 [M^+].

Synthesis of 5-[4-(3,5-dibromostyryl)-2,5-di(decyloxy)styryl]-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene (**9**)

The same procedure was followed as described for the synthesis of **6**, starting from *Kt*-BuO (96.1 μ mol; 10.8 mg), **7** (96.1 μ mol; 107 mg) and 3,5-dibromobenzaldehyde **5** (96.1 μ mol; 25.4 mg). The crude product was dissolved in THF and precipitated in MeOH resulting in a yellow solid (83.4 mg, yield = 70%).

mp 72-74°C; ; $[\alpha]_D^{20} = +7.03 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL}$ ($c = 0.9 \text{ g/100 ml}$ in THF); ^1H NMR (300 MHz, CDCl_3 , δ): 7.57 (s, 2H, Ar H), 7.52 (s, 1H, Ar H), 7.42 (d ($J = 16.5 \text{ Hz}$), 1H, CH), 7.32 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.10 (s, 1H, Ar H), 7.05 (s, 1H, Ar H), 7.04 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.00 (d ($J = 16.5 \text{ Hz}$), 1H, CH), 6.74 (s, 2H, Ar H), 4.05-3.97 (m, 10 H, CH_2), 1.88-1.47 (m, 20H, CH_2 , CH), 1.38-1.15 (m, 42H, CH_2), 0.97-0.92 (m, 9H, CH_3), 0.87 (m, 24H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , δ): 153.4, 151.3, 150.8, 141.8, 138.4, 133.0, 132.3, 129.5, 128.0, 127.9, 126.6, 125.7, 125.3, 123.2, 122.4, 111.0, 110.3, 105.3, 73.6, 69.2, 67.8, 67.7, 39.3, 39.2, 37.4, 37.3, 36.5, 32.0, 31.9, 30.4, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 28.0, 26.2, 24.9, 24.7, 22.7, 22.7, 22.6, 22.6, 19.9, 19.8, 14.1; APCIMS $m/z = 1636 [M^+]$.

Synthesis of 5-(3,5-dibromostyryl)-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene (**10**)

The same procedure was followed as described for the synthesis of **6**, starting from *Kt*-BuO (2.32 mmol; 260 mg), **2** (2.32 mmol; 896 mg) and **3** (2.32 mmol; 1.33 g). The crude product was dissolved in THF and precipitated in MeOH resulting in a yellow, viscous oil (319 mg, yield = 31%).

$[\alpha]_D^{20} = -5.24 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL}$ ($c = 2.5 \text{ g/100 ml}$ in THF); ; ^1H NMR (300 MHz, CDCl_3 , δ): 7.55 (s, 2H, Ar H), 7.52 (s, 1H, Ar H), 7.01 (d ($J = 16.2 \text{ Hz}$), 1H, CH), 6.80 (d ($J = 16.2 \text{ Hz}$), 1H, CH), 6.70 (s, 2H, Ar H), 4.04 (m, 6H, CH_2), 1.87-1.52 (m, 12H, CH_2 , CH), 1.32-1.16 (m, 18H, CH_2), 0.94-0.85 (m, 27H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , δ): 153.4, 141.1, 139.0, 132.4, 131.8, 131.4, 127.9, 142.5, 123.2, 105.4, 71.8, 67.5, 39.4, 39.3, 37.4, 36.4, 29.8, 29.7, 28.0, 24.8, 24.7, 22.7, 22.6, 19.6; APCIMS $m/z = 808 [M^+]$.

Synthesis of 2,5-di((*S*)-3,7-dimethyloctyloxy)-1,4-di(diethoxy phosphonylmethyl)benzene (**12**)

Paraformaldehyde (39.0 mmol; 1.17 g) was added to a solution of **11** (13.0 mmol; 5.10 g) and HBr (14 ml, 33% solution in acetic acid) in CH_3COOH (20 ml) and was further stirred for 1h at 60°C under nitrogen atmosphere. After cooling to room temperature, the precipitate was filtered off and washed with H_2O , a saturated NaHCO_3 -solution, MeOH and dried in vacuo to

give a white solid. Next, P(OEt)₃ (30 ml) was added and the mixture was stirred overnight at 150°C and under an argon atmosphere. After reaction the excess of triethylphosphite and ethyl bromide were removed under reduced pressure and crude product was further purified by column chromatography (silica gel; eluent: EtOAc) to give a viscous, pale yellow oil (3.87 g, yield = 42%).

$[\alpha]_D^{20} = -7.05 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{mL}$ ($c = 3.1 \text{ g/100 ml}$ in CHCl₃); ¹H NMR (300 MHz, CDCl₃, δ): 6.87 (s, 2H, Ar H), 4.02-3.89 (m, 12H, CH₂), 3.17 (d ($J = 20.4 \text{ Hz}$), 4H, CH₂), 1.82-1.42 (m, 8H, CH₂, CH), 1.30-1.10 (m, 24H, CH₃, CH₂), 0.89 (d, 6H, CH₃), 0.82 (d, 12H, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 150.4, 119.4, 114.8, 67.3, 61.9, 39.3, 37.4, 36.5, 09.9, 28.0, 26.2 (d $J = 138 \text{ Hz}$), 22.7, 19.7, 16.4; CIMS $m/z = 691 [M^+]$.

Synthesis of diethyl 2,5-di((*S*)-3,7-dimethyloctyloxy)-4-[3,4,5-tri(octyloxy)styryl]benzylphosphonate (**14**)

The same procedure was followed as described for the synthesis of **6**, starting from Kt-BuO (1.00 mmol; 112 mg), **12** (1.00 mmol; 691 mg) 3,4,5-(trioctyloxy)benzaldehyde **13** (1.00 mmol; 491 mg). The crude product was further purified by column chromatography (silica gel; eluent: EtOAc/*n*-heptane (4/6)) to give a pale yellow viscous oil (257 mg, yield = 25%).

$[\alpha]_D^{20} -4.55 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{mL}$ ($c = 4.4 \text{ g/100 ml}$ in THF); ¹H NMR (300 MHz, CDCl₃, δ): 7.33 (d ($J = 16.1 \text{ Hz}$), 1H, CH), 7.04 (s, 1H, Ar H), 6.97 (d ($J = 16.1 \text{ Hz}$), 1H, CH), 6.96 (s (br), 1H, Ar H), 6.71 (s, 2H, Ar H), 4.09-3.95 (m, 14H, CH₂), 3.25 (d ($J = 21.9 \text{ Hz}$), 2H, CH₂), 1.91-1.41 (m, 20H, CH₂, CH), 1.36-1.14 (m, 48H, CH₂, CH₃), 0.99-0.92 (m, 6H, CH₃), 0.90-0.83 (m, 21H, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 153.2, 151.0, 150.4, 138.2, 133.2, 128.7, 125.9, 122.7, 120.4, 115.8, 109.4, 105.2, 73.4, 69.0, 67.5, 67.2, 61.8, 39.3, 37.4, 37.3, 36.5, 36.4, 31.9, 31.8, 30.4, 30.1, 29.9, 29.6, 29.5, 29.4, 29.3, 28.0, 27.9, 26.1, 24.7, 22.7, 22.6, 22.6, 25.6, 25.5, 19.8, 19.7, 16.4, 14.0; APCIMS $m/z = 1028 [M^+]$.

Synthesis of 5-[4-(3,5-dibromostyryl)-2,5-di((*S*)-3,7-dimethyloctyloxy) styryl]-1,2,3-tri(octyloxy)benzene (**15**)

The same procedure was followed as described for the synthesis of **6**, starting from *Kt*-BuO (923 μmol ; 106 mg), **14** (923 μmol ; 948 mg) and 3,5-dibromobenzaldehyde **5** (923 μmol ; 244 mg). The crude product was dissolved in THF and precipitated in MeOH resulting, in a yellow solid (455 mg, yield = 44%).

mp 72-73°C; $[\alpha]_{\text{D}}^{20} = -3.33 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{mL}$ ($c = 1.5 \text{ g}/100 \text{ ml}$ in THF); ^1H NMR (300 MHz, 22.7, 22.6, 22.6, 22.6, 19.9, 19.2, 14.1; APCIMS $m/z = 1137 [M^+]$. CDCl_3 , δ): 7.56 (s (br), 2H, Ar H), 7.51 (s, 1H, Ar H), 7.42 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.32 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 7.10 (s, 1H, Ar H), 7.05 (s, 1H, Ar H), 7.04 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 6.99 (d ($J = 16.4 \text{ Hz}$), 1H, CH), 6.73 (s, 2H, Ar H), 4.12-3.95 (m, 10H, CH_2), 1.97-1.44 (m, 20H, CH_2 , CH), 1.41-1.11 (m, 14H, CH_2), 0.99 (d, 6H, CH_3), 0.89-0.83 (m, 21H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , δ): 153.3, 151.4, 150.8, 141.8, 138.4, 133.0, 132.3, 129.5, 128.0, 127.9, 126.6, 125.7, 125.3, 123.2, 122.4, 111.0, 110.2, 105.3, 73.6, 69.2, 67.8, 67.7, 39.3, 39.2, 37.4, 37.3, 36.5, 31.9, 31.8, 30.4, 30.2, 29.6, 29.5, 29.4, 29.3, 28.0, 26.2, 24.9, 24.7,

Polymer Synthesis

Synthesis of **P1**

To a suspension of CuO (11.9 μmol ; 945 μg) and $\text{Pd}(\text{PPh}_3)_4$ (2.97 μmol ; 3.41 mg) in DMF (4 ml), purged with argon and shielded from the light was added **8** (59.3 μmol ; 97.0 mg) and **16** (59.3 μmol ; 32.7mg), dissolved in toluene (10 ml). The mixture was heated to 100°C and stirred overnight. After cooling to room temperature, the crude polymer was precipitated in cold MeOH. The polymer was washed with acetone using a Soxhlet apparatus to remove any side products. Finally, the polymer was extracted with CHCl_3 , precipitated in MeOH and dried in vacuo (41.3 mg, yield CHCl_3 -fraction = 41%).

Synthesis of **P2**

The same procedure was followed as described for the synthesis of **P1**, starting from CuO (11.2 μmol ; 885 μg), $\text{Pd}(\text{PPh}_3)_4$ (2.78 μmol ; 3.20 mg), **9** (55.5 μmol ; 67.8 mg) and **16** (55.5 μmol ; 30.7mg) in DMF/toluene (3 ml/8 ml). The crude product was precipitated in MeOH

and subsequently washed with MeOH and acetone via Soxhlet extractions. In a final step the polymer was washed with pentane, the solvent was removed in vacuo. The polymer was redissolved in THF and precipitated in MeOH and dried under reduced pressure (25.5 mg, yield pentane-fraction = 36%).

Synthesis of **P3**

To a suspension of Pd(PPh₃)₄ (1.64 μmol; 2.00 mg) and CuO (6.56 μmol; 521 μg) in DMF (3 ml), purged with argon and shielded from the light was added **9** (32.8 μmol; 40.0 mg) and **17** (32.8 μmol; 15.3 mg), dissolved in THF (12 ml). The mixture was heated to 66°C and stirred overnight. After cooling to room temperature, the crude polymer was precipitated in cold MeOH. Next, the polymer was washed with methanol and acetone using a Soxhlet apparatus. In a final step the polymer washed with pentane, the solvent was removed in vacuo. The polymer was redissolved in THF, precipitated in MeOH and dried under reduced pressure (19.2 mg, yield pentane-fraction = 49%).

Synthesis of **P4**

The same procedure was followed as described for the synthesis of **P3**, starting from Pd(PPh₃)₄ (3.10 μmol; 3.60 mg), CuO (12.4 μmol; 986 μg), **10** (62.0 μmol; 50.0 mg) and **17** (62.0 μmol; 28.9) in DMF/THF (2 ml/8 ml). The crude product was precipitated in MeOH and subsequently washed with MeOH and acetone via Soxhlet extractions. In a final step the polymer was dissolved in pentane, precipitated in MeOH and dried under reduced pressure (23.7 mg, yield pentane-fraction = 49%).

Synthesis of **P5**

The same procedure was followed as described for the synthesis of **P1**, starting from CuO (6.55 μmol; 525 μg), Pd(PPh₃)₄ (1.65 μmol; 2.00 mg), **15** (33.3 μmol; 37.9 mg) and **16** (33.3 μmol; 18.4 mg) in DMF/toluene (3 ml/10 ml). The polymer was precipitated in MeOH and subsequently washed with MeOH and acetone via Soxhlet extractions. In a final step the polymer was washed with pentane and subsequently, the solvent was removed in vacuo. The

polymer was redissolved in THF, precipitated in MeOH and dried under reduced pressure (16.9 mg, yield pentane-fraction = 42%).

Synthesis of **P6**

The same procedure was followed as described for the synthesis of **P3**, starting from Pd(PPh₃)₄ (2.20 μmol; 2.50 mg), CuO (8.80 μmol; 700 μg), **15** (44.0 μmol; 50.0 mg) and **17** (44.0 μmol; 20.4) in DMF/THF (1 ml/6 ml). The polymer was precipitated in MeOH and subsequently washed with MeOH and acetone via Soxhlet extractions. In a final step the polymer was washed with pentane, the solvent was removed in vacuo. The polymer was redissolved in THF, precipitated in MeOH and dried in vacuo (39.0 mg, yield pentane fraction = 79%).

Results and Discussion

Synthesis of the Polymers

In total 6 polymers were prepared. The polymers vary in the aromatic group between the *meta*-phenylene linkage, the length of the OPV side chain and the place where the chiral alkyl group was incorporated. Concerning the connecting aromatic group, both 3,3'-dimethoxybithiophene and thienothiophene were considered. Due to the presence of S-O interactions, the bithiophene adopts a planar conformation.^[27] As a consequence, both groups connect the phenylene groups in a linear way, so no additional kinks are introduced. The length of the OPV was varied, since this inherently alters the optical contribution of the OPV substituent. The location where the chiral alkyl groups are introduced on the OPV (at the periphery or lateral) was varied as this might affect the chiral expression.

The synthesis of the OPVs with the chiral side-chains located at the periphery is depicted in Scheme 1. The synthesis of **8** starts with the coupling of dialdehyde **1** with phosphonate **2** via a Wittig Horner reaction, yielding **6**. In a next step, using a Wittig Horner reaction, **6** was coupled with **7**, which was formed by the Wittig Horner coupling of diphosphonate **4** with chiral gallic aldehyde **3**, resulting in **8**. In order to shorten the length of the OPV chain, **7** was

coupled with 3,5-dibromobenzaldehyde **5**, via a Wittig Horner reaction, resulting in **9**. Further decreasing the length of the OPV was done by directly coupling the chiral gallic aldehyde **3** with phosphonate **2**, by means of a Wittig Horner reaction, yielding **10**. The synthesis of the OPV side-chains with lateral chiral alkyl chains is depicted in Scheme 2 and starts with the conversion of chiral dialkoxybenzene **11** to diphosphonate **12**, via a bromomethylation of **11**, followed by an Arbuzov reaction. Diphosphonate **12** was then coupled with achiral gallic aldehyde **13**, by means of a Wittig Horner reaction, resulting in **14**. Reaction of **14** with aldehyde **5**, via a Wittig Horner reaction finally resulted in **15**. The Stille coupling reaction was used as polymerization method, using Pd(PPh₃)₄ as catalyst and CuO as co-catalyst. The desired dibrominated OPV was coupled with either the distannylated bithiophene **16** or the distannylated thienothiophene **17** to yield **P1-P6** (Scheme 3). Removing the byproducts was done with methanol and/or acetone using a Soxhlet apparatus. Finally, **P1** was extracted with CHCl₃, precipitated in methanol and dried under reduced pressure. **P2-P6** were extracted with pentane. After removing the solvent, the polymers were redissolved in THF, precipitated in methanol and dried in vacuo. The molar mass and polydispersity of **P1-P6** were determined by GPC in THF toward polystyrene standards (Table 1).

Chiroptical Properties

If the UV-vis spectra of the polymers are considered (**Figure 2**), it is clear that a contribution from both the polymer backbone and the OPV side chain is present. The polymer backbone absorbs near 550 or 480 nm depending on the linker used (bithiophene or thienothiophene, respectively). λ_{max} and extinction coefficient of the OPV moiety obviously depends on its length. In contrast to *e.g.* regioregular poly(3-alkylthiophene), the UV-vis spectra of **P1-P6** only slightly change if the solvent quality is decreased. This can be attributed to the fact that the OPV is already planar in good solvent. The conjugation length does thus not significant increases; the major difference is the change of the dielectric constant of the medium, affecting the extinction coefficient. In addition, the stacking of the OPVs, either in a helical

structure or by aggregation of the polymer backbones, can give rise to an altered extinction coefficient. Concerning the backbone, the *meta*-linkage disrupts the conjugation, irrespective of the conformation of the backbone.

Concerning the chiral expression, it is clear that none of the polymers shows Cotton effects in good solvent, reflecting the disordered coil-like state. In poor solvent mixtures **P1-P3**, in which the chiral entities are present at the peripheral gallic acid moiety, do not show any Cotton effects. As will be shown, **P1-P3** aggregate in poor solvents. Chirality will be expressed if the polymer backbones do not adopt a parallel orientation towards each other, but are rotated (and always in the same direction). The reason why the backbones become rotated is the steric hindrance from the asymmetric branching of the chiral side chain. However, if the environment around the chiral centers is not sterically demanding, for instance because they are located far from the main chain, this driving force becomes too small to induce this rotation and the concomitant chiral stacking. This might explain the absence of Cotton effects of **P1-P3** in poor solvent.

In order to prove this hypothesis, **P4** was prepared. In this polymer, the chiral centers are located as closely as possible to the polymer backbone. The polymer adopts a helical conformation in poor solvent (see further). The proximity of the asymmetric centers to the backbone results in this polymer in the presence of Cotton effects. The position of the zero-crossing – centered in the absorption band of the OPV chromophore - and the bisignate shape clearly point at a chiral orientation of the side-chain, invoked by the one-handed helical backbone (see also **Figure 4**).

The above-mentioned hypothesis on the effect of the position of the chiral centers on the chiral expression was further tested in **P5-P6**. In these polymers the chiral centers are located lateral of the OPV. The CD spectra in poor solvent again show clear Cotton effects. The CD spectra of **P5** show, apart from a contribution in the absorption region of the OPV side-chain, also a response in the region of the polymer backbone. This is in line with the fact that the

polymers aggregate in poor solvent (see later), as both side and main chain are chirally stacked (Figure 4). The Cotton effects in **P6** are less intense. Because the main and side chain absorb in regions that are quite close to each other – in the UV-vis spectrum they more or less overlap –, no separate Cotton effects can be distinguished.

Next, it is investigated whether the polymers fold into a helical structure upon decreasing the solvent quality, or that they aggregate. For this purpose, the influence of the concentration on the UV-vis and CD spectra (if Cotton effects are present) was investigated in a solvent mixture in which intermediate spectra are found. If the polymer folds into a helical structure, which is an intramolecular transition, no concentration dependency is found, while in case of aggregation, a concentration-dependency is observed. The spectra are present in SI (Figure S1-S6) and show that, except for **P4**, all polymers aggregate. This might seem surprising, as the molecular structure, more in particular the *meta*-linkage and the presence of the gallic acid moiety, should favor a helical conformation, which is indeed found for **P4**. The fundamental difference between **P4** and the other polymers is the presence of (long) lateral alkyl groups (decyl in **P1-P3**, branched octyl in **P5-P6**). As shown in **Figure 3**, this results in severe steric hindrance in case a helical conformation would be adopted, while a nice planar structure with optimal alkyl packing that allows stacking of multiple polymer chains, can be formed. This is perfectly in line with previous results of OPV-functionalized poly(dithienopyrrole)s.^[25]

DSC

Finally, some DSC experiments were performed to verify the chiroptical results. The T_m 's are summarized in **Table 1**. T_m was typically determined from the second heating run at a heating rate of 20°C/min. From these results it can be concluded that all the polymers that aggregate, as shown by the UV-vis and CD experiments, also have a melting peak and, thus, are semicrystalline. Only **P4**, that forms a helix, has no melting peaks. Hence, it can be concluded that the DSC experiments confirm the chiroptical results.

Supramolecular Behavior

The supra- and macromolecular behavior of the polymers is schematically shown in Figure 4. In good solvent, all polymers are present as disordered coil-like structures. Upon decreasing the solvent quality, the preferred process seems the folding into a helical structure. However, if long alkyl groups are present lateral of the OPV side chain, the formation of this helical structure is impeded and the polymers adopt a planar, extended chain and stack. If the chiral side-chains are located on the gallic acid moiety and the OPV contains as least 3 phenyl rings, the asymmetric C-atom are too far from the backbone to induce a chiral stacking. Combined, this result in aggregation of **P1-P3** with parallel oriented polymer chains. **P4** folds into a one-handed helix and orients the pendant OPV side-chains in a chiral way. **P5-P6**, finally, aggregate in a chiral way.

Conclusion

A series of *meta*-coupled arylenes, equipped with chiral, conjugated OPV side-chains, was synthesized. The distance between two consecutive OPV side chains was changed by either using a bithiophene or thienothiophene unit as linker. Also, the length of the OPV side-chain, as well as the placement of the chiral moieties on the OPV side-chains, was varied. Chiroptical studies reveal that the expression of chirality depends on the position of the chiral moieties on the OPV side-chain. Chirality is only expressed in **P4-P6**, as they bear their chiral centers in β -position of the main chain. **P1-P3**, on the other hand, form achiral supramolecular stacks, as the distance from the chiral centers to the polymer main chain is too large. Second, only **P4** forms a helical structure in the appropriate conditions. As for the other polymers, a planar, supramolecular structure is obtained, as the (a)chiral lateral alkoxy chains prevent the folding into a helical conformation, due to sterical reasons. These results were verified by DSC measurements.

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Figure 1. General structure of the polymers studied.

Figure 2. UV-vis and CD spectra of the polymers in different solvent conditions. A) + B) **P1** ($c = 1.4 \cdot 10^{-5}$ M); C) + D) **P2** ($c = 1.1 \cdot 10^{-5}$ M); E) + F) **P3** ($c = 1.8 \cdot 10^{-5}$ M); G) + H) **P4** ($c = 1.9 \cdot 10^{-5}$ M); I) + J) **P5** ($c = 2.7 \cdot 10^{-5}$ M); K) + L) **P6** ($c = 3.7 \cdot 10^{-5}$ M).

Figure 3. Visualization of the packing of the lateral alkyl groups in **P3** (A and B) in a helical or extended conformation and **P4** (C) in a helical conformation.

Good solvent

Poor solvent

- * Long OPV
- * Lateral placement of chiral moieties

- * Short OPV
- * Chiral moieties at periphery

- * long OPV
- * Chiral moieties at periphery

Figure 4. Schematic representation of the proposed supra- and macromolecular behavior of the polymers in poor solvent.

Scheme 1. Synthesis of the OPVs with the chiral alkyl chains located at the periphery. Conditions: $i)$ $\text{K}^t\text{-BuO}$, THF, rt.

Scheme 2. Synthesis of OPV with lateral chiral alkyl chains. Conditions: *i)* 1) $(\text{CH}_2\text{O})_n$, HBr , 60°C ; 2) $\text{P}(\text{OEt})_3$, 150°C ; *ii)* Kt-BuO , THF , rt .

Scheme 3. Synthesis of **P1-P6**. Conditions: *i)* Pd(PPh₃)₄, CuO, Toluene/DMF, 100°C; *ii)* Pd(PPh₃)₄, CuI, THF/DMF, reflux.

Table 1. Mn, D and Tm of **P1-P6**.

polymer	M _n ^{a)} [kg/mol]	D ^a	T _m ^{b)} [°C]
P1	12.7	1.2	69
P2	9.9	1.2	71
P3	10.6	1.3	76
P4	8.3	1.3	/
P5	8.9	1.3	66
P6	13.4	1.3	71

^{a)} determined by GPC in THF toward poly(styrene) standards; ^{b)} determined by DSC at a heating rate of 20K/min

Conjugated polymers with different oligo(phenylene vinylene) (OPV) side chains are prepared. It is investigated how the length of the OPV side chain and the placement of chiral substituents influences the optical properties, the supramolecular structure and the chiral expression

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Conformational Behavior of Conjugated Polymers With Oligo(phenylene vinylene) Side chains

Supporting Information

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Conformational behavior of conjugated polymers with oligo(phenylene vinylene) side chains

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Dilution experiments for P1-P6

Figure S1: Dilution experiment of **P1** in THF/MeOH (6/4).

Figure S2: Dilution experiment of **P2** in THF/MeOH (3/7).

Figure S3: Dilution experiment of **P3** in $CHCl_3/MeOH$ (3/7).

Figure S4: Dilution experiment of **P4** in $CHCl_3/MeOH$ (5/5): A) UV-vis and B) CD spectra.

Dilution experiment of **P5** in THF/MeOH (4/6): A) UV-vis and B) CD spectra.

Dilution experiment of **P6** in THF/MeOH (55/45): A) UV-vis and B) CD spectra.

^1H and ^{13}C NMR

^1H NMR and ^{13}C spectra of (*E*)-2,5-di(decyloxy)-4-(3,5-dibromostyryl)benzaldehyde (**6**)

Figure S7: ^1H NMR (CDCl_3) of **6**.

Figure S8: ^{13}C NMR (CDCl_3) of **6**.

^1H NMR and ^{13}C spectra of diethyl-2,5-di(decyloxy)-4-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)styryl]benzylphosphonate (**7**)

Figure S9: ^1H NMR (CDCl₃) of **7**.

Figure S10: ^{13}C NMR (CDCl₃) of **7**.

^1H NMR and ^{13}C spectra of 5-[4-[4-(3,5-dibromostyryl)-2,5-di(octyloxy)styryl]-2,5-di(octyloxy)styryl]-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene (**8**)

Figure S11: ^1H NMR (CDCl_3) of **8**.

Figure S12: ^{13}C NMR (CDCl_3) of **8**.

^1H NMR and ^{13}C spectra of 5-[4-(3,5-dibromostyryl)-2,5-di(decyloxy)styryl]-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene (**9**)

Figure S13: ^1H NMR (CDCl_3) of **9**.

Figure S14: ^{13}C NMR (CDCl_3) of **9**.

^1H NMR and ^{13}C spectra of 5-(3,5-dibromostyryl)-1,2,3-tri((*S*)-3,7-dimethyloctyloxy)benzene
(10)

Figure S15: ^1H NMR (CDCl_3) of **10**.

Figure S16: ^{13}C NMR (CDCl_3) of **10**.

^1H NMR and ^{13}C spectra of 2,5-di((*S*)-3,7-dimethyloctyloxy)-1,4-di(diethoxy phosphonylmethyl)benzene (**12**)

^1H NMR and ^{13}C spectra of diethyl 2,5-di((*S*)-3,7-dimethyloctyloxy)-4-[3,4,5-tri(octyloxy)styryl]benzylphosphonate (**14**)

Figure S19: ^1H NMR (CDCl_3) of **14**.

Figure S20: ^{13}C NMR (CDCl_3) of **14**.

^1H NMR and ^{13}C spectra of 5-[4-(3,5-dibromostyryl)-2,5-di((*S*)-3,7-dimethyloctyloxy)styryl]-1,2,3-tri(octyloxy)benzene (**15**)

Figure S21: ^1H NMR (CDCl_3) of **15**.

Figure S22: ^{13}C NMR (CDCl_3) of **15**.

¹H NMR of **P1**.

Figure S23: ¹H NMR (CDCl₃) of **P1**.

¹H NMR of **P2**.

Figure S24: ¹H NMR (CDCl₃) of **P2**.

^1H NMR of **P3**.

Figure S25: ^1H NMR (CDCl_3) of **P3**.

^1H NMR of **P4**.

Figure S26: ^1H NMR (CDCl_3) of **P4**.

^1H NMR of **P5**.

Figure S27: ^1H NMR (CDCl_3) of **P5**.

^1H NMR of **P6**.

Figure S28: ^1H NMR (CDCl_3) of **P6**.