

Steering the Conformation and Chiroptical Properties of Poly(dithienopyrrole)s Substituted with Chiral OPV Side Chains.

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Received December 15, 2009; Revised Manuscript Received January 18, 2010

ABSTRACT: This manuscript discusses the conformation and chiroptical properties of poly(dithienopyrrole)s (PDTPs), substituted with oligo(phenylenevinylene) (OPV) side chains and the influence of the substitution of the OPV moiety on these features. The OPV side chains were equipped with gallic acid moieties in order to promote the formation of a helical conformation in poor solvents. The polymers were prepared by Stille-couplings and characterized by GPC and NMR, UV–vis, CD, and emission spectroscopy. It was found that OPV–PDTPs, solely equipped with (chiral) alkyl groups at the terminal gallic acid group, show a very strong tendency to adopt a helical conformation, but no resolution of the mixture of helices and therefore no chiral expression. Additional substitution of the OPV allows for a discrimination of the mixture of helical senses. In this way, the OPV side chains can be chirally organized by the helical PDTP backbone. Substitution of the OPV in α -position, however, sterically excludes the possibility to adopt a helical conformation, but results in a lamellar supramolecular structure in poor solvents. The macromolecular behavior is explained in terms of space confinement and steric hindrance in the respective structures.

Introduction

Conjugated polymers have been extensively studied and implemented as active materials in, for instance, transistors, organic light-emitting diodes, and solar cells.¹ Although most conjugated polymers are equipped with substituents, the optical and electronic properties of the material typically originate from the conjugated backbone. The substituents, usually aliphatic groups, can indeed ensure a good solubility and even promote the formation of a particular supramolecular, for instance lamellar, structure, but they normally do not contribute to the polymer's optical or electronic properties.

Poly(dithieno[3,2-b:2',3'-d]pyrrole) (PDTP),² are a particularly interesting class of conjugated polymers, as they show high conjugation lengths, can easily be oxidized and remain oxidized for prolonged periods of time. Substitution on the N atom with sufficiently bulky alkyl groups renders them soluble.^{2e-h} Moreover, the nature of the substituent also plays a crucial role in the macromolecular and supramolecular structure of the polymers in poor solvents. If (branched) alkyl groups are used, the polymer strands stack.^{2g} In contrast, if a tri(alkyl)-substituted gallic acid moiety is employed, the combination of space confinement, π -stacking and van der Waals interactions favors a helical conformation.^{2h} This difference becomes even more clear if chiral substituents are employed. In the former case, aggregates, composed of chirally stacked (planar) polymer chains are obtained, giving rise to chiral effects in the absorption band of the polymer backbone. In the latter case, the chirality of the substituents, together with proper space confinement and the rigidity of the benzene moiety, results in an efficient discrimination of the two enantiomeric helices³ and a one-handed helical backbone, decorated with the gallic acid substituents, is obtained. In this

way, the gallic acid substituents are chirally organized by the onehanded helical PDTP backbone. This is, for instance, expressed in the circular dichroism (CD) spectra, which also show a contribution originating from this group.

It is clear that the presence of this gallic acid moiety results in (*i*) a one-handed helical conformation of the backbone, which, on its turn, can organize the substituent; and (*ii*) a contribution of the substituent to the optical and electronic properties of the polymer. Nevertheless, the contribution of the side chain remains limited in the sense that it does not absorb in the visible, but UV region. However, the contribution of the substituent (in the absorption range of the polymer) could be significantly enhanced if side chains with much larger conjugation lengths, such as oligo(phenylenevinylene) (OPV), are employed. Furthermore, the absorption of the side chain can be tuned in such way that it allows an efficient energy transfer to the polymer backbone. Moreover, this approach also provides a possibility to chirally align conjugated oligomers by the helical backbone.

This manuscript reports on the synthesis and chiroptical properties of PDTPs, equipped with OPVs. The OPVs are functionalized by gallic acid moieties in order to promote a possible formation of a helical conformation in poor solvents, but differ in the amount of solubilizing alkoxy-groups. The influence of the substitution on the OPV side chain on the conformation and chiroptical properties of the polymers is studied. Figure 1 shows structures of polymers Pa-Pc.

Experimental Section

Materials and Instrumentation. All starting materials were purchased from Acros Organics, Fluka, Merck, or Aldrich and were used as received. *N*,*N*-Dimethylformamide (DMF), toluene, and THF were dried by distillation over calcium hydride, molecular sieves, and Na/K, respectively. Gel permeation chromatography

Published on Web 02/04/2010

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Figure 1. Structure of the polymers.

(GPC) measurements were done in tetrahydrofuran (THF) as eluent toward polystyrene standards with a Shimadzu 10A apparatus equipped with a tunable absorbance detector and a differential refractometer. ¹H and ¹³C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. UV-vis spectra were measured on a Varian Cary 400 or a Perkin-Elmer Lambda 40 UV/vis spectrophotometer; the CD spectra were recorded with and a JASCO 62 DS apparatus. The DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus. Optical rotation was done on a Polaar 20; the concentration (in g/100 mL) and solvent used are given in parentheses. PL emission spectra were taken on a Fluorolog-3 FL3-22 spectrometer from Horiba Yobin Yvon. PL quantum efficiencies (Φ_{PL}) were determined using relative measurements with fluorescence references. The absorbance of the solutions used to determine the fluorescence quantum yields and excitation spectra did not exceed 0.1 at the excitation wavelength. All solutions were degassed prior to the emission experiments. The fluorescence decay times were determined using a single photon timing setup described in detail elsewhere.⁴ The frequency doubled output (488 nm, 4.09 MHz, 1.2 ps fwhm) of a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) was used as vertically polarized excitation light. The fluorescence was via a polarizer (magic angle) and focused on a monochromator (Sciencetech 9030) and detected with a microchannel plate (R3809U, Hamamatsu). Data acquisition was done using a time correlated single photon card (TCSPC PC card, SPC 630, Becker & Hickl GmbH, Germany). The experimental instrument response function was on the order of 50 ps. Decays were collected in 4096 channels. The decays were analyzed globally with a time-resolved fluorescence analysis (TRFA) software, based on iterative reconvolution and a nonlinear least-squares approach. The fitting was judged by the value of the reduced χ^2 parameter and also by the appearance of the residuals and the autocorrelation function of the residuals.

1b, 6 **3a**, 7 **4a**, 8 **4b**, 9 **6**, 10 and **7**¹¹ were synthesized according to literature procedures.

Synthesis

Synthesis of the OPV–DTP, 9a and 9b. Synthesis of (+)-2,5-Di(bromomethyl)-1,4-di((S)-2-methylbutoxy)benzene (2b). Paraformaldehyde (4.07 g, 136 mmol) was added to a solution of HBr (45 mL, 33% in AcOH) and 1b (11.3 g, 45.2 mmol) in AcOH (200 mL). After being stirred at 60 °C for 1 h, the reaction mixture was allowed to cool down and subsequently filtered. The precipitate was washed with H₂O, an aqueous NaHCO₃ solution, H₂O, and MeOH and dried under reduced pressure, yielding white crystals.

Yield: 14.0 g (71%).

 $[\alpha]_{D}^{20} = +5.0 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} (c = 1.6 \text{ in THF}).$ ${}^{1}\text{H NMR (CDCl_3): } \delta = 6.84 (s, 2\text{H}), 4.53 (s, 4\text{H}), 3.80$ (m, 4H), 1.90 (m, 2H), 1.60 (m, 2H), 1.29 (m, 2H), 1.06 (d, 6H), 0.97 (t, 6H).

¹³C NMR (CDCl₃): $\delta = 150.8$, 127.5, 114.4, 73.6, 50.8, 35.0, 29.9, 26.3, 16.8, 11.5

MS: $m/z = 911 (2 \times M + K^+)$

Synthesis of (+)-2,5-Di((S)-2-methylbutoxy)-1,4-di(diethoxyphosphonylmethyl)benzene (3b). A mixture of 2b (14.0 g, 32.1 mmol) in triethylphosphite (100 mL) was refluxed under an argon atmosphere for 3 h. After removal of ethyl bromide and triethylphosphite under reduced pressure, a colorless solid was obtained, which was used without further purification.

Yield: 16.9 g (96%).

Mp: 62-65 °C.

 $\begin{bmatrix} \alpha_{\rm D}^{120} = +6.9 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} \ (c = 6.1 \text{ in THF}). \\ ^{1}\text{H} \text{ NMR } (\text{CDCl}_{3}): \ \delta = 6.92 \ (\text{s}, \ 2\text{H}), \ 4.01 \ (\text{m}, \ 8\text{H}), \ \end{cases}$ 3.73 (m, 4H), 3.23 (d, J = 20.1 Hz, 4H), 1.85 (m, 2H),1.57 (m, 2H), 1.30 (m, 2H), 1.23 (t, 12H), 1.02 (d, 6H), 0.94 (t, 6H).

Synthesis of 5a. Under argon atmosphere, a solution of 3a (4.16 g, 11.0 mmol) in dry THF (10 mL) was added to a suspension of NaH (0.260 g, 11.0 mmol) in dry THF (20 mL). The mixture was refluxed for 5 min, after which a solution of **4a** (5.74 g, 10.0 mmol) in dry THF (10 mL) was added. The reaction mixture was refluxed for an additional 2 h and was allowed to cool down. An aqueous HCl solution (1 M, 20 mL) and CH₂Cl₂ were added and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with an aqueous NaHCO3 solution and H2O and dried over MgSO₄. After removal of the organic solvents under reduced pressure, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂ and CH₂Cl₂/MeOH 95/5), resulting in a colorless oil.

Yield: 2.55 g (32%)

 $[\alpha]_D^{20} = -4.33 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (*c* = 4.2 in THF).

¹H NMR (CD₂Cl₂): δ = 7.49 (d, J = 8.2 Hz, 2H), 7.31 (dd, J = 8.2 Hz, 1.8 Hz, 2H), 7.05 (s, 2H), 6.77 (s, 2H), 4.05 (m, 10H), 3.13 (d, J = 21.9 Hz, 2H), 1.85 (m, 6H), 1.60 (m, 6H), 1.31 (m, 18H), 1.17 (t, 6H), 0.88 (d, 6H), 0.84 (d, 3H), 0.83 (d, 18H).

¹³C NMR (CDCl₃): $\delta = 153.7, 138.4, 136.4, 132.9, 131.6,$ 131.4, 130.5, 129.1, 127.4, 126.7, 105.1, 71.9, 67.5, 62.4, 39.7, 37.8, 36.9, 34.7, 32.8, 30.2, 28.4, 25.2, 23.0, 22.8, 19.8, 16.6. MS: $m/z = 822.2 (M^+ + Na^+)$.

Synthesis of 5b. The same procedure was followed as described for the synthesis of 5a, starting from 3b (5.00 g, 9.10 mmol), NaH (0.218 g, 9.10 mmol), and 4b (4.46 g, 9.10 mmol). The crude product was purified by column chromatography (SiO₂, hexane/EtOAc 1/1) and isolated as a pale yellow, green fluorescent solid.

Yield: 1.91 g (24%).

Mp: 28-31 °C.

 $[\alpha]_{D}^{20} = +2.6 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 1.1 in THF).

H NMR (CD₂Cl₂): δ = 7.36 (d, J = 16.4 Hz, 1H), 7.07 (s, 1H), 7.01 (d, J=16.4 Hz, 1H), 6.92 (d, J=2.7 Hz, 1H), 6.72 (s, 2H), 3.91 (m, 14H), 3.21 (d, J = 22.0 Hz, 2H), 1.76 (m, 10 H), 1.48 (m, 6H), 1.32 (m, 26H), 1.24 (t, 6H), 1.07 (d, 3H), 1.05 (d, 3H), 0.97 (t, 3H), 0.97 (t, 3H), 0.88 (t, 9H).

¹³C NMR (CD₂Cl₂): δ = 153.7, 151.5, 151.4, 150.8, 138.3, 133.6, 128.8, 126.2, 126.1, 122.8, 121.2, 121.1, 116.5, 74.7, 74.1, 73.7, 69.2, 62.2, 62.1, 35.6, 35.5, 32.4, 32.3, 30.8, 30.0, 29.9, 29.8, 26.8, 26.6, 23.1, 16.9, 16.8, 16.7, 16.6, 14.3, 11.7. MS: $m/z = 1796 (2 \times M + Na^{+}).$

Synthesis of N-(4-Formylfenyl)dithieno[3,2-b:2',3'-d]pyrrole (8). A mixture of 7 (3.44 g, 10.6 mmol), NaOt-Bu (2.43 g, 25.4 mmol), Pd₂dba₃ (0.242 g, 0.265 mmol) (dba = dibenzylidene acetone), and DPPF (0.588 g, 1.06 mmol) (DPPF = diphenylphosphinoferrocene) in dry toluene (50 mL) was purged with argon for 15 min, after which a solution of 6 (1.84 g, 11.0 mmol) in dry toluene (10 mL) was added. After being refluxed for 19 h, the reaction mixture was allowed to cool down and H₂O was added. The aqueous layer was extracted with Et₂O twice and the solvents of the combined organic layers were removed under reduced pressure. The residue was dissolved in THF (100 mL) and an aqueous HCl solution (1.0 M, 50 mL) was added. This mixture was stirred vigorously at room temperature for 1.5 h. Next, Et₂O (150 mL) was added and the organic layer was washed with aqueous NaHCO3 and NaCl solutions. Purification of the crude product by column chromatography (SiO₂, CH₂Cl₂/hexane 8/2) yielded a yellow solid.

Yield: 1.03 g (34%).

Mp: 186-190 °C.

¹H NMR (CDCl₃): $\delta = 10.05$ (s, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.24 (s, 4H).

Synthesis of 9a. A solution of 5a (5.70 g, 7.10 mmol) in dry, argon purged THF (15 mL) was added to a suspension of NaH (0.170 g, 7.10 mmol) and 8 (1.84 g, 6.50 mmol) in dry, argon purged THF (10 mL). The reaction mixture was refluxed for 1 h, and after the mixture had cooled down, CH₂Cl₂ (30 mL) and an aqueous HCl solution (1 M, 20 mL) were added. The organic and aqueous layers were separated and the latter was again extracted with CH₂Cl₂ (30 mL). The combined organic layers were dried over MgSO₄, and after removal of the solvents, purification by column chromatography (SiO₂, CH₂Cl₂) yielded a yellow solid.

Yield: 1.02 g (55%).

Mp: 76–77 °C $[\alpha]_{D}^{20} = -6.03 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} (c = 3.3 \text{ in THF}).$ ¹H NMR (CD₂Cl₂): $\delta = 7.70 \text{ (d, } J = 8.2 \text{ Hz, 2H}), 7.61 \text{ (d, } J = 8.2 \text{ Hz, 2H})$ 8.2 Hz, 2H), 7.54 (s, 4H), 7.22 (s, 4H), 7.19 (s, 2H), 7.08 (d, J= 16.4 Hz, 1H), 7.02 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H), 3.96 (m, 6H), 1.71 (m, 12H), 1.26 (m, 18H), 0.97 (d, 6H), 0.93 (d, 3H), 0.88 (d, 18H).

¹³C NMR (CD₂Cl₂): δ = 153.7, 144.1, 139.2, 138.4, 137.3, 136.7, 135.4, 132.8, 129.2, 128.7, 128.0, 127.6, 127.4, 127.2, 127.0, 123.9, 122.8, 117.3, 112.7, 105.1, 72.0, 67.6, 39.7, 37.7, 36.8, 30.2, 28.3, 25.1, 22.8, 19.7.

MS: m/z = 928 (M⁺).

Synthesis of 9b. The same procedure as described for 9a was followed, starting from 5b (1.77 g, 2.00 mmol), NaH (48.0 mg, 2.00 mmol) and 8 (0.514 g, 1.82 mmol). The product was isolated as yellow solid.

Yield: 1.27 g (69%).

Mp: 107-109 °C

¹H NMR (CD₂Cl₂): $\delta = 7.71$ (d, J = 9.1 Hz, 2H), 7.61 (d, J =9.1 Hz, 2H), 7.55 (d, J = 16.4 Hz, 1H), 7.41 (d, J = 16.4 Hz, 1H), 7.25 (s, 4H), 7.24 (d, J=16.4 Hz, 1H), 7.18 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H), 4.01 (t, 4H), 3.91 (m, 6H), 1.99 (m, 2H), 1.82 (m, 4H), 1.68 (m, 4H), 1.37 (m, 32H), 1.24 (d, 3H), 1.12 (d, 3H), 1.02 (t, 6H), 0.89 (t, 9H).

¹³C NMR (CD₂Cl₂): δ = 153.6, 151.6, 151.3, 144.2, 139.0, 138.2, 136.1, 133.4, 129.0, 127.9, 127.7, 127.3, 126.6, 123.8, 122.9, 122.5, 117.2, 112.7, 110.8, 110.1, 104.8, 74.7, 74.4, 73.7, 69.2, 35.5, 35.4, 32.2, 30.6, 29.9, 29.8, 29.7, 29.6, 26.7, 26.4, 23.0, 17.0, 16.9, 14.2, 11.7, 11.5.

MS: $m/z = 1016 (M^+)$

Synthesis of the OPV-DTP 9c. Synthesis of (+)-2,5-Di((S)-2-methoxy)benzaldehyde (12c). Under nitrogen atmosphere, a solution of 2,5-dihydroxybenzaldehyde 10 in dry DMF (20 mL) was added dropwise to a suspension of NaH (2.38 g, 99.0 mmol) in dry DMF (80 mL). Next, 11

(16.4 g, 109 mmol) was added, and the mixture was stirred at 55 °C for one night. Water was carefully added and the aqueous layer was extracted with hexane (2×100 mL). The combined organic layers were dried over MgSO₄, and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) , yielding a pale yellow liquid.

Yield: 4.20 g (31%)

 $[\alpha_{\rm DD}^{20} = +14.8 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} (c = 1.5 \text{ in THF}).$ ¹H NMR (CD₂Cl₂): $\delta = 10.49$ (s, 1H), 7.31 (d, J = 2.7 Hz, 1H), 7.12 (dd, J=2.7 Hz, J=9.1 Hz), 6.92 (d, J=9.2 Hz, 1H), 3.81 (m, 4H), 1.88 (m, 2H), 1.57 (m, 2H), 1.28 (m, 2H), 1.04 (d, 3H), 1.00 (d, 3H), 0.96 (t, 3H), 0.94 (t, 3H)

¹³C NMR (CD₂Cl₂): δ = 189.5, 156.7, 153.5, 125.5, 123.9, 114.6, 111.1, 74.1, 73.8, 35.2, 35.1, 26.4, 16.7, 16.7, 11.4.

MS: $m/z = 279 (M^+)$, 209 (M⁺ - C₅H₁₀), 138 (M⁺ - C₁₀H₂₁). Synthesis of (+)-2,5-Di((S)-2-methylbutoxy)-4-nitrobenzaldehyde (13c). A solution of 12c (5.40 g, 19.7 mmol) and $CuSO_4 \cdot 5H_2O$ (17.0 mg, 70.0 μ mol) in acetic acid anhydride (50 mL) was stirred at 45 °C for 48 h. After cooling the reaction mixture to 10 °C, an aqueous HNO₃ solution (1.90 mL, 70%) was added dropwise while keeping the temperature in the range of 10-15 °C. After being stirred for an additional hour at this temperature, the reaction mixture was extracted with Et₂O (2 \times 50 mL) and the combined organic layers were washed with an aqueous solution of NaHCO₃ and H₂O. After removal of the solvent under reduced pressure, the residue was dissolved in THF (50 mL) and an aqueous NaOH (1 M, 30 mL) was added. The reaction mixture was stirred vigorously at room temperature for 2 h and then extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with aqueous HCl (1 M), a NaHCO₃ solution and H₂O. Purification of the crude product by column chromatography (SiO₂, EtOAc/ hexane 1/9) yielded a yellow solid.

Yield: 4.30 g (68%).

Mp: 64-66 °C

 $[\alpha]_{D}^{20} = +9.8 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 6.7 in THF).

H NMR (CDCl₃): $\delta = 10.50$ (s, 1H), 7.51 (s, 1H), 7.40 (s, 1H), 3.92 (m, 4H), 1.92 (m, 2H), 1.56 (m, 2H), 1.31 (m, 2H), 1.06 (d, 3H), 1.02 (d, 3H), 0.94 (m, 6H)

¹³C NMR (CDCl₃): δ = 188.2, 154.6, 146.0, 143.7, 127.6, 113.5, 109.9, 74.9, 74.3, 34.7, 34.6, 26.1, 25.9, 16.5, 16.4, 11.3.

MS: $m/z = 324 (M^+)$, $254 (M^+ - C_5 H_{10})$, $184 (M^+ - C_{10} H_{20})$ Synthesis of 14c. A solution of 5b (0.531 g, 0.600 mmol) in

dry THF (10 mL) was added to a suspension of NaH (14.4 mg, 0.600 mmol) and 13c (0.177 g, 0.546 mmol) in dry THF (5 mL). After 2 h of reflux, an aqueous HCl solution (1 M) was added. The aqueous layer was extracted with Et₂O (2 \times 30 mL) and the combined organic layers were washed with an aqueous NaHCO₃ solution and H₂O. After drying over MgSO₄, the organic solvents were removed and purification of the crude product with column chromatography (SiO_2 , CH_2Cl_2 /hexane 1/1) yielded an orange solid.

Yield: 2.47 g (80%).

Mp: 75-78 °C

 $[\alpha]_{D}^{20} = +1.0 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 24.3 in THF).

H NMR (CD₂Cl₂): $\delta = 7.66$ (d, J = 17.4 Hz, 1H), 7.48 (d, J = 17.4 Hz, 1H), 7.45 (s, 1H), 7.39 (d, J = 16.4 Hz, 1H), 7.32 (s, 1H), 7.18 (s, 1H), 7.14 (s, 1H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.74 (s, 2H), 4.00 (t, 6H), 3.89 (m, 8H), 1.97 (m, 4H), 1.82 (m, 4H), 1.66 (m, 6H), 1.36 (m, 34H), 1.04 (m, 24H), 0.88 (t, 9H).

^bC NMR (CD₂Cl₂): $\delta = 153.6, 151.8, 151.3, 149.8, 147.9,$ 138.3, 137.9, 134.2, 133.3, 129.5, 128.2, 127.3, 126.2, 122.3, 121.2, 112.0, 110.5, 110.3, 109.7, 104.9, 75.0, 74.6, 74.5, 73.7, 69.2, 35.4, 35.1, 32.2, 30.7, 29.9, 29.8, 29.7, 29.6, 26.7, 26.6, 26.4, 26.2, 23.0, 16.9, 16.8, 16.5, 14.2, 11.6, 11.5, 11.4.

MS: $m/z = 1079 (M + Na^+)$.

Synthesis of 15c. Tin(II) chloride (2.16 g, 11.4 mmol) was added to a solution of 14c (1.50 g, 1.42 mmol) in EtOAc/ EtOH 1/1 (20 mL). This mixture was refluxed for 45 min, after which another portion of tin(II) chloride (0.216 g, 1.14 mmol) was added. The reaction mixture was refluxed for an additional h and then poured in an aqueous NaOH solution (1 M, 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were washed with an aqueous NaHCO3 solution and water. The solvents were removed under reduced pressure and the residue was dissolved in Et₂O. A few drops of HCl (37%) were added, resulting in precipitation of the product as its ammonium salt, which was filtered off and washed with Et₂O. An aqueous solution of NaOH (1 M) and Et₂O was added and the aqueous layer was extracted with Et₂O. After drying the combined organic layers over MgSO₄, the solvents were removed, yielding a yellow solid.

Yield: 1.04 g (71%).

Mp: 96-98 °C.

 $[\alpha]_{D}^{20} = +5.7 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 8.6 in THF). ¹H NMR (CD₂Cl₂): δ = 7.46 (d, J = 16.4 Hz, 1H), 7.38 (d, J = 16.4 Hz, 1H), 7.27 (d, J = 16.4 Hz, 1H), 7.16 (s, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 7.04 (d, J = 16.4 Hz, 1H), 6.73 (s, 2H), 6.32 (s, 1H), 3.87 (m, 16H), 1.90 (m, 8H), 1.65 (m, 6H), 1.38 (m, 34H), 1.03 (m, 24H), 0.87 (m, 9H).

¹³C NMR (CD₂Cl₂): δ = 153.6, 152.1, 151.5, 151.0, 141.4, 138.0, 133.6, 128.5, 128.2, 125.8, 123.5, 122.7, 118.4, 116.6, 110.5, 109.5, 109.0, 104.7, 100.7, 74.7, 74.6, 74.4, 74.0, 73.7, 69.2, 35.5, 35.2, 32.3, 32.2, 30.7, 29.9, 29.8, 29.7, 26.7, 26.6, 26.5, 23.0, 16.9, 16.7, 14.2, 11.6, 11.4.

MS: $m/z = 1026 (M^+)$.

Synthesis of 9c. The same procedure as described for 8 was followed, starting from 7 (0.304 g, 0.94 mmol), NaOtBu (0.217 g, 2.26 mmol), Pd₂dba₃ (21.5 mg, 23.5 µmol), DPPF (52.0 mg, 94.0 µmol), and 15c (0.960 g, 0.940 mmol) in dry, argon purged, toluene. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂/petroleum ether), yielding a yellow solid.

Yield: 0.378 g (34%)

Mp: 53-55 °C

 $[\alpha]_{D}^{20} = +0.7 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (*c* = 18.0 in THF). ¹H NMR (CD₂Cl₂): δ = 7.58 (s, 2H), 7.41 (s, 1H), 7.41 (d, J = 16.4 Hz, 1H, 7.22 (s, 1H), 7.15 (s, 1H), 7.14 (d, J = 5.5 Hz, 2H), 7.08 (d, J=16.4 Hz, 1H), 7.04 (s, 1H), 6.98 (d, J=5.5 Hz, 2H), 6.75 (s, 2H), 4.02 (t, 4H), 3.82 (m, 10H), 1.98 (m, 3H), 1.73 (m, 10H), 1.37 (m, 35H), 1.05 (m, 18H), 0.89 (t, 9H), 0.75 (t, 3H), 0.75 (d, 3H).

¹³C NMR (CD₂Cl₂): δ = 153.7, 151.6, 151.5, 151.3, 147.9, 145.7, 138.3, 133.5, 129.1, 128.4, 127.3, 127.2, 123.8, 123.0, 122.6, 122.5, 116.3, 113.5, 111.9, 111.8, 110.4, 105.0, 74.9, 74.7, 74.6, 73.8, 69.3, 35.6, 35.4, 35.1, 32.4, 32.3, 30.8, 30.0, 29.8, 26.8, 26.7, 26.6, 26.3, 23.1, 17.1, 17.0, 16.9, 16.6, 14.3, 11.7.11.3.

MS: $m/z = 1212 (M + Na^+ + 2H)$

Synthesis of the Monomers. Synthesis of 16a. N-Bromosuccinimide (NBS) (0.430 g, 2.42 mmol) was added to an ice cooled solution of 9a (1.00 g, 1.10 mmol) in CHCl₃ (5 mL), shielded from light. After stirring the mixture for 15 min at 0 °C and for 1 h at room temperature, an aqueous NaHSO₃ solution was added. The aqueous layer was extracted twice with CH2Cl2. The combined organic layers were washed with an aqueous NaHCO3 solution and H2O and dried over $MgSO_4$. Purification by column chromatography (SiO₂, CH_2Cl_2 /hexane 1/1) yielded a yellow solid.

Yield: 0.857 (72%)

Mp: 84-85 °C

 $[\alpha]_{D}^{20} = -5.12 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 3.3 in THF).

¹H NMR (CD₂Cl₂): $\delta = 7.69$ (d, J = 8.2 Hz, 2H), 7.54 (s, 4H), 7.50 (d, J=8.2 Hz, 2H), 7.24 (s, 2H), 7.19 (s, 2H), 7.08 (d, J = 16.4 Hz, 1H), 7.01 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H),4.01 (m, 6H), 1.71 (m, 12H), 1.24 (m, 18H), 0.97 (d, 6H), 0.92 (d, 3H), 0.87 (d, 18H).

 3 C NMR (CD₂Cl₂): $\delta = 153.6, 140.8, 138.4, 138.1, 137.4,$ 136.5, 136.2, 132.7, 129.2, 128.1, 127.3, 127.2, 127.0, 123.0, 117.1, 116.0, 110.7, 105.0, 72.0, 67.6, 39.7, 39.6, 37.9, 36.8, 30.2, 30.1, 28.3, 25.1, 22.8, 22.7, 19.8, 19.7.

MS: $m/z = 1086 (M^+)$.

Synthesis of 16b. The same procedure as described for compound 16a was followed, starting from 9b (0.810 g, 0.800 mmol) and NBS (0.320 g, 1.80 mmol) in CHCl₃ (8 mL). The product was isolated as a yellow solid.

Yield: 0.721 (77%)

Mp: 120-124 °C

 $[\alpha]_{D}^{20} = +0.6 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 5.1 in THF).

 $z^{1}H$ NMR (CD₂Cl₂): $\bar{\delta} = 7.69$ (d, J = 8.2 Hz, 2H), 7.56 (d, J = 16.4 Hz, 1 H), 7.50 (d, J = 8.2 Hz, 2 H), 7.41 (d, J = 16.4 Hz,1H), 7.25 (s, 2H), 7.23 (d, J = 16.4 Hz, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H), 4.02 (t, 4H), 3.91 (m, 6H), 2.00 (m, 2H), 1.81 (m, 4H), 1.78 (m, 4H), 1.68 (m, 4H), 1.37 (m, 32H), 1.14 (d, 3H), 1.12 (d, 3H), 1.02 (t, 6H), 0.89 (t, 9H).

³C NMR (CD₂Cl₂): $\delta = 153.6, 151.6, 151.3, 140.9, 138.2,$ 138.0, 136.9, 133.4, 129.1, 128.0, 127.4, 126.4, 124.3, 123.1, 122.4, 117.1, 116.0, 110.8, 110.7, 110.0, 104.8, 74.6, 74.4, 73.7, 69.2, 35.5, 35.4, 32.2, 30.7, 30.0, 29.9, 29.8, 29.7, 26.8, 26.7, 26.5, 23.0, 17.0, 16.9, 14.2, 11.7, 11.7.

MS: m/z = 1173 (M⁺), 1013 (M⁺ - 2 × Br).

Synthesis of 16c. The same procedure as described for compound 16a was followed, starting from 9c (0.596 g, 0.500 mmol) and NBS (0.196 g, 1.10 mmol) in CHCl₃ (10 mL). Instead of stirring the mixture for 1 h at room temperature, this reaction mixture was kept at 0 °C for 45 min. A yellow solid was obtained.

Yield: 0.511 (76%)

Mp: 106-108 °C

 $[\alpha]_D^{20} = -1.08 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (*c* = 3.7 in THF). ¹H NMR (CD₂Cl₂): δ = 7.57 (s, 2H), 7.41 (d, *J* = 16.4 Hz, 1H), 7.39 (s, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 16.4 Hz, 1H), 7.01 (s, 2H), 6.96 (s, 1H), 6.75 (s, 2H), 4.02 (t, 4H), 3.80 (m, 10H), 1.99 (m, 3H), 1.67 (m, 11H), 1.37 (m, 29H), 1.05 (m, 18H), 0.89 (t, 9H), 0.78 (m, 6H).

¹³C NMR (CD₂Cl₂): δ = 153.7, 151.6, 151.5, 151.2, 147.8, 142.3, 138.4, 133.6, 129.2, 128.0, 127.5, 127.2, 127.1, 124.3, 122.6, 122.3, 116.8, 116.2, 111.7, 110.5, 110.4, 110.0, 105.1, 74.8, 73.8, 69.3, 35.7, 35.5, 35.2, 32.5, 32.4, 30.9, 30.1, 30.0, 29.9, 26.9, 26.8, 26.4, 23.2, 17.2, 17.0, 16.7, 14.5, 11.9, 11.4. MS: $m/z = 1368 (M^+ + Na^+)$.

Synthesis of 17a. The same procedure as described for compound 16a was followed, starting from 9a (0.300 g, 0.320 mmol) and N-iodosuccinimide (NIS) (0.158 g, 0.704 mmol) in $CHCl_3$ (3 mL). The crude product was purified by column chromatography (SiO₂, CH₂Cl₂/hexane 1/1), yielding a yellow solid.

Yield: 0.294 (78%).

Mp: 96-98 °C

 $[\alpha]_{D}^{20} = -5.16 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$ (c = 8.9 in THF).

H NMR (CDCl₃): $\delta = 7.69$ (d, J = 8.2 Hz, 2H), 7.54 (s, 4H), 7.50 (d, J=8.2 Hz, 2H), 7.38 (s, 2H), 7.18 (s, 2H), 7.08 (d, J = 16.4 Hz, 1H), 7.01 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H), 3.02 (m, 6H), 1.70 (m, 12H), 1.27 (m, 18H), 0.97 (d, 6H), 0.92 (d, 3H), 0.87 (d, 18H).

¹³C NMR (CD₂Cl₂): δ = 153.6, 142.9, 138.5, 138.2, 137.3, 136.5, 136.0, 132.8, 129.2, 129.1, 128.1, 127.3, 127.2, 127.0,

122.8, 121.9, 121.6, 105.1, 72.0, 71.8, 67.6, 39.7, 37.9, 37.7, 36.8, 30.2, 30.1, 28.3, 25.1, 22.9, 22.8, 19.8.

MS: $m/z = 1180 (M^+)$.

Synthesis of 18a. A solution of n-BuLi in hexane (2.5 M, 0.300 mL, 0.755 mmol) was added to an ice cooled, with argon purged solution of 16a (0.400 g, 0.37 mmol) in dry $Et_2O(8 mL)$. After the mixture was stirred for 15 min at 0 °C, Bu₃SnCl (0.240 mL, 0.869 mmol) was added. The reaction mixture was allowed to slowly reach room temperature and was stirred at room temperature for one night. The solvent was removed under reduced pressure and hexane was added to the residue. After filtration and removal of the organic solvents in vacuo, a yellow, viscous oil was obtained.

Yield: 0.535 g (96%)

 $[\alpha]_{D}^{20} = +8.46 \text{ deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} (c = 0.4 \text{ in THF}).$ ¹H NMR (CDCl₃): $\delta = 7.71 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.64 (d, J = 8.2 \text{ Hz}).$ 8.2 Hz, 2H), 7.55 (s, 4H), 7.20 (s, 4H), 7.08 (d, J = 16.4 Hz, 1H), 7.02 (d, J=16.4 Hz, 1H), 6.75 (s, 2H), 4.02 (m, 6H), 1.71 (m, 24H), 1.23 (m, 46H), 0.89 (m, 47H).

MS: $m/z = 1218 (M^+ - SnC_{12}H_{24}), 929 (M^+ - 2 \times$ $SnC_{12}H_{24}$).

Synthesis of 18b. The same procedure as described for 18a was used, starting from 16b (0.300 g, 0.256 mmol) in dry Et₂O (12 mL), n-BuLi (0.215 mL, 2.5 M in hexane, 0.538 mmol) and Bu₃SnCl (0.153 mL, 0.560 mmol). The product was isolated as a yellow, viscous oil.

Yield: 0.394 g (97%)

¹H NMR (\tilde{CDCl}_3): $\delta = 7.71$ (d, J = 8.2 Hz, 2H), 7.63 (d, J =8.2 Hz, 2H), 7.55 (d, J = 16.4 Hz, 1H), 7.41 (d, J = 16.4 Hz, 1H), 7.25 (d, J = 16.4 Hz, 1H), 7.21 (s, 2H), 7.18 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 16.4 Hz, 1H), 6.75 (s, 2H), 4.02 (t, 4H), 3.91 (m, 6H), 2.00 (m, 2H), 1.82 (m, 4H), 1.59 (m, 18H), 1.32 (m, 46H), 1.08 (m, 12H), 0.89 (m, 39H).

Synthesis of 18c. The same procedure as described for 18a was used, starting from 16c (0.300 g, 0.223 mmol) in dry Et₂O, *n*-BuLi (0.187 mL, 2.5 M in hexane, 0.468 mmol), and Bu₃SnCl (0.140 mL, 0.515 mmol). The crude product was dissolved in CH₂Cl₂ (2 mL), precipitated in cold MeOH $(-78 \,^{\circ}\text{C})$ and filtered cold. At room temperature, the product is present as a dark yellow, viscous oil.

Yield: 0.299 g (76%)

¹H NMR (\dot{CDCl}_3): $\delta = 7.58$ (s, 2H), 7.42 (s, 1H), 7.41 (d, J = 16.4 Hz, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 16.4Hz, 1H), 7.05 (s, 1H), 6.96 (s, 2H), 6.75 (s, 2H), 4.02 (t, 4H), 3.83 (m, 10H), 1.98 (m, 3H), 1.87 (m, 4H), 1.60 (m, 27H), 1.33 (m, 44H), 1.06 (m, 29H), 0.89 (m, 28H), 0.77 (m, 6H).

Synthesis of the Polymers. Synthesis of Pa. A solution of 18a (0.301 g, 0.200 mmol) and 17a (0.236 g, 0.200 mmol) in dry, argon purged toluene (15 mL) was added to a suspension of CuO (0.200 mmol, 16.0 mg) and Pd(PPh₃)₄ (10.0 μ mol, 11.8 mg) in dry, argon purged DMF (15 mL). After the mixture was purged for 30 min, it was refluxed for 13 h. The polymer was precipitated in MeOH, filtered off, and fractionated by Soxhlet extraction with subsequently MeOH, 1,4-dioxane under reduced pressure, and THF. The THF fraction, being the higher molecular-mass fraction, was concentrated in vacuo and added dropwise to MeOH. The precipitate was filtered off and dried under reduced pressure, resulting in a black solid.

Yield: 0.317 g (86%).

Synthesis of **Pb**. The same procedure as described for **Pa** was used, starting from a solution of 18b (0.254 g, 0.160 mmol) and 16b (0.188 g, 0.160 mmol) in dry, argon purged toluene (12 mL) and a solution of CuO (12.7 mg, 0.160 mmol) and Pd(PPh₃)₄ (8.0 μ mol, 9.2 mg) in dry, argon purged DMF (12 mL). The polymer was fractionated by Soxhlet extraction with acetone, hexane, and THF. The polymer (=THF fraction) was isolated as a black solid.

Yield: 81.5 mg (25%).

Synthesis of Pc. The same procedure as described for Pa was used, starting from a solution of 18c (0.299 g, 0.169 mmol) and 16c (0.227 g, 0.169 mmol) in dry, argon purged toluene (13 mL) and a solution of CuO (13.4 mg, 0.169 mmol) and Pd(PPh₃)₄ (8.4 µmol, 9.7 mg) in dry, argon purged DMF (13 mL). The polymer is fractionated by Soxhlet extraction with acetone, 1,4-dioxane under reduced pressure and THF. The polymer (=THF fraction) was isolated as a black solid.

Yield: 43.8 mg (11%).

Results and Discussion

Synthesis of the Dithienopyrroles. The synthesis of the OPV-functionalized DTP-building blocks for the preparation of Pa and Pb is depicted in Scheme 1. The key reaction is the Wittig-Horner coupling between the phosphonate 5a,b and the benzaldehyde-functionalized DTP 8. ¹H NMR spectroscopy confirmed the *E*-configuration of the double bond. The synthesis of **5a**, **b** is straightforward and starts with a double bromomethylation of the alkylated hydroquinone 1b and subsequent Arbuzov reaction, yielding the bis-(phosphonate) 2b. A Wittig-Horner reaction using equimolar amounts of the aldehyde **4a**,**b** and bis(phosphonate)s 3a,b resulted in the targeted 5a,b. 8, in its turn, was prepared by a Buchwald-Hartwig reaction of the acetal-protected p-aminobenzaldehyde and 7 and subsequent deprotection of the aldehyde functionality.

When employing a similar procedure to prepare 9c, we experienced great difficulties with the Buchwald-Hartwig reaction of 7 and the corresponding dialkoxy-derivative of 6 (i.e., 2-(4-amino-2,5-dialkoxyphenyl)-1,3-dioxalane), which could be attributed to the instability of the latter compound. Therefore, an alternative strategy was used (Scheme 2), in which the formation of such very electron-rich aniline derivative was avoided. After alkylation of 10, 12c was nitrated, and this aldehyde was coupled to the phosphonate 5b, building the OPV moiety. Then, the nitro functionality was reduced to the amine using SnCl₂. Finally, the OPVfunctionalized DTP was formed by a Buchwald-Hartwig reaction.

Polymer Synthesis and Characterization. The polymers were prepared using a Stille-coupling, since, compared with other polymerization methodologies, such as chemical or electrochemical oxidation, this method produces PDTPs with the highest molar mass and allows optimal control of the molecular structure.^{2g} It was preferred to use diiodated DTPs as dihalogenated monomers, but, unfortunately, reaction with N-iodosuccinimide (NIS) and 9, was only successful for 9a (Scheme 3). Because the dibromation of 9 (with N-bromosuccinimide (NBS)) could, in contrast, readily be performed on 9a-c, Pa was prepared using diiodated DTP (17a), while Pb-c were synthesized from the dibromated DTP monomers (16b-c). The distannylated monomers were prepared from 16a-c in a two-step process, consisting of a Li-Br exchange reaction using n-BuLi and quenching the dilithium salt with Bu₃SnCl. The polymerization was performed using Pd[PPh₃]₄ as a catalyst in the presence of CuO.¹² After polymerization and precipitation, the polymers were washed with several solvents (see Experimental Section) using a Soxhlet extraction apparatus in order to remove byproduct and oligomers; typically, the THF-soluble fraction, being the highest-molar mass fraction, was used for further experiments.

Scheme 1. Synthesis of the OPV-DTP 9a,b^a



^a Conditions: (i) HBr (33% in AcOH), p-formaldehyde, (ii), P(OEt)₃, (iii) NaH, and (iv) (1) Pd₂dba₃, DPPF, NaOtBu, (2) H₃O⁺.

Scheme 2. Synthesis of the DTP $9c^{a}$



^a Conditions: (i) NaH, DMF; (ii) (1) Ac₂O, CuSO₄, (2) HNO₃ (70%); (3) NaOH, H₂O, (iii) NaH; (iv) SnCl₂; (v) Pd₂dba₃, DPPF, NaOtBu.

The molar mass of the polymers was determined by GPC in THF toward polystyrene standards. The number-averaged molar mass (M_n) amounts to 17, 9.8, and 18 kg/mol for **Pa**, **Pb**, and **Pc**, respectively. The polydispersities were rather low for a polycondensation (1.5, 1.7, and 1.2), which can be

attributed to the intensive fractionation. DSC experiments revealed no melting, nor glass transition, nor degradation below 250 °C. Finally, the ¹H NMR spectrum of the polymers (Supporting Information) showed no defects, nor end-groups, indicative for a regular structure and a relatively high

Scheme 3. Synthesis of the DTP $9c^a$



^a Conditions: (i) NBS; (ii) NIS; (iii) (1) n-BuLi, (2) Bu₃SnCl; (iv) Pd[PPh₃]₄, CuO.

degree of polymerization, which is in line with the choice of polymerization reaction.

UV-Vis and CD Spectroscopy. The UV-vis spectra of Pa, Pb, and Pc in a good (THF) and poor solvent (THF/hexane or THF/Et₂O mixtures) and the corresponding CD spectra in a poor solvent are displayed in Figure 2b,c. No (or very small) Cotton effects are observed in a good solvent. For comparison, also the spectra of Pgal (Figure 2a) are incorporated. As previously indicated,^{2g} the spectra of Pgal are composed of three transitions: one near 270 nm with corresponding bisignate Cotton effects in poor solvent, arising from the gallic acid substituent, one near 350 nm with corresponding monosignate Cotton effect in poor solvent, originating from a localized $\pi - \pi^*$ transition of the polymer backbone around 600 nm, which is CD silent.

Naturally, as the conjugation length of the side chain in **Pa**-**Pc** is increased compared with **Pgal**, also its λ_{max} and extinction coefficient increase. If the spectrum of **Pa** is considered, the absorption near 370 nm is in fact a superposition of the OPV absorption and the localized backbone transition. Apart from the shifted side chain absorption, also the delocalized transition of the backbone differs from that of **Pgal** in THF. Decreasing the solvent quality (Figure 2b) further shifts the spectra. However, a spectrum wherein the low-energy absorption band resembles that of **Pgal** in a THF—in which the polymer is present as (unordered)

coils-can be obtained if a dichlorobenzene solution is heated (Figure 3). It is clear that Pa adopts a coil-like conformation in hot dichlorobenzene, but that it folds into a helical conformation or stacks upon cooling and further decreasing the solvent quality. Intermediate spectra are obtained in o-dichlorobenzene at room temperature. The fact that a clear isosbestic point is observed suggests that the transition is a one-step process. In order to discriminate between the two possible transitions (coil-helix or coilaggregate), the concentration dependence of the UV-vis spectrum in *o*-dichlorobenzene was investigated (Figure S1, see Supporting Information), which demonstrates that the transition occurs intramolecularly, as is also the case for **Pgal**. On the other hand, two differences in the conformational behavior of **Pgal** and **Pa** can be observed. First, it can be concluded that Pa shows a far stronger tendency to fold into a helical structure than Pgal as, in conditions in which Pgal solely adopts a coil-like state (THF, chloroform, dichlorobenzene, ..., at room temperature), Pa is already partially present as helices. This can be attributed by the increased π -interactions of the OPV side chain compared with the gallic acid substituent, which favors the helical conformation. A similar behavior has already been observed for OPV-functionalized poly(ureidophthalimide)s.13 A second difference can be observed from the CD spectra in poor solvents: while the chiral substituent in Pgal can discriminate between both helical senses, resulting in Cotton effects, no



Figure 2. (a) Structure of **Pgal**, (b) UV-vis spectra of **Pgal**, **Pa**, **Pb**, and **Pc** in a good solvent, (c) UV-vis spectra of **Pgal**, **Pa**, and **Pb** in a poor solvent and (d) CD spectra of **Pgal**, **Pa**, **Pb**, and **Pc** in a poor solvent. $(c_{Pgal} = 0.35 \text{ g/L}, c_{Pa} = 0.30 \text{ g/L}, c_{Pb} = 0.30 \text{ g/L}, and c_{Pc} = 0.70 \text{ g/L})$.

Cotton effects are observed for **Pa**, indicating that a racemic mixture of both helical enantiomers is formed. This loss of



Figure 3. Thermochromism of Pa in *o*-dichlorobenzene (c = 0.15 g/L).

chiral discrimination can be attributed to the reduced space filling around the chiral alkyl chains—similar to that in chirally substituted *cis*-poly(thiophene)s, which also adopt a (wide) helical conformation, resulting in insufficient chiral discrimination.¹⁴

In order to increase the chiral discrimination, **Pb**, in which the chiral substituents are located closer to the polymer backbone, was prepared. In this way, the space filling around the chiral moieties is more demanding and the chirality of the alkyl groups has an increased ability to discriminate between both helical senses.

A comparison of the UV-vis spectra of Pa and Pb shows that the absorption band of the OPV substituent is redshifted and that, consequently, this absorption and the localized absorption of the backbone appear as two separate bands. From the solvatochromism and the clear presence of an isosbestic point (Figure 4) it can again be concluded that two different states are possible, *i.e.*, (unordered) coils and a helix or aggregates. Although still some residual absorption of the helix/aggregate is visible in neat THF at room temperature, it is clear that Pb shows a stronger tendency to adopt a coil conformation than **Pa**, which can be attributed to the increased steric hindrance accompanying the introduction of the additional alkoxy groups. Importantly, also some (small) Cotton effects can be observed in a poor solvent mixture. Analogously to Pgal, a bisignate Cotton effect is observed in the absorption band of the substituent. Moreover, the high-energy backbone absorption also shows a (small) monosignate Cotton effect, as is the case for Pgal. The presence of such (negative) monosignate Cotton effect, centered near 350 nm, can be argued from the lower intensity of the positive lobe of the bisignate Cotton effect compared with the negative lobe: in that case, the Cotton effect near 350 nm is a superposition of the positive lobe of a bisignate Cotton effect and a negative monosignate Cotton effect. The delocalized backbone transition is-similar to that for Pgal—CD silent.^{2h}

A second step in the chiroptical characterization again consists of the determination whether a helical conformation or aggregates are formed in poor solvents. Therefore, the concentration dependence of the UV–vis and CD spectra was investigated in solvent conditions in which intermediate spectra are observed (*i. e.*, THF/Et₂O (1/1)) (Supporting Information, Figure S2). This experiment demonstrates that also **Pb** shows a coil–helix transition. As a consequence, it can be concluded that both the conformational behavior and the ability of chiral discrimination of **Pb** resembles those of **Pgal**. Furthermore, it also shows a coil–helix transition and the chiral substituents can discriminate between both helical senses.



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Figure 4. Solvatochromism of Pb in THF/Et₂O mixtures: (a) UV-vis and (b) CD spectra (c = 0.30 g/L).

If, finally, the UV-vis and CD spectra of Pc are examined, it is obvious that completely different spectra are obtained. In a good solvent, the UV-vis spectrum is not a superposition of two different states, instead, it strongly resembles the spectrum of **Pgal** in chloroform. The fact that **Pc**, in contrast to **Pa** and **Pb**, is solely present as unordered coils in THF can be attributed to the increased steric hindrance, originating from the additional alkyl groups. In poor solvents, the UV-vis spectrum, especially the region assignable to the backbone transition, undergoes significant changes, as, for instance, a sharp low-energy band near 660 nm appears. In addition, strong Cotton effects are observed.

In order to further investigate this, again the dependence of the UV-vis and CD spectra on the solvent composition was investigated (Figure 5). Next, the concentration dependence of the spectra was evaluated in a solvent mixture (THF/Et₂O (1/1)) in which intermediate spectra are observed, which revealed that the transition is concentration dependent (Supporting Information, Figure S3). Therefore, it must be concluded that the observed transition does not occur intramolecularly, but intermolecularly, i.e. no helical conformation is formed, but the polymer strands stacks.

In summary, the UV-vis and CD experiments demonstrate that **Pa** and **Pb** both adopt a helical conformation in a poor solvent mixture, while **Pc** instead aggregates. In good solvent conditions, all polymers tend to adopt an unordered coil-like conformation. For **Pc**, this is the case in THF, while **Pa** and, to a smaller extent, **Pb**, are present as a mixture of both conformations in those conditions. Concerning the

Figure 5. Solvatochromism of Pc in THF/Et₂O mixtures: (a) UV-vis and (b) CD spectra (c = 35 mg/L).

chiral discrimination, chirality is expressed in both **Pb** and **Pc**, but is absent in **Pa**.

Emission Spectroscopy. In order to confirm the proposed conformational behavior of the polymers, their emission spectra and fluorescence decays were measured in good and poor solvents. In Figure 6, the emission spectra of 9b,c in THF and Pgal in toluene and THF, which serve as model compounds for the OPV side chain and the polymer backbone in **Pb** and **Pc**, respectively, are shown, together with the emission spectra of Pb and Pc in THF and THF/Et₂O (1/9). Because of the difficulty to force Pa into the nonhelical state, this polymer was not further studied. While the decays of the fluorescence of 9b,c at 480 (excitation at 375 nm) could be analyzed as single exponential decay, the fluorescence decays of Pgal, Pb, and Pc were generally more complex both for excitation at 375 nm (OPV-side chains) and 550 nm (backbone). The fluorescence lifetimes and quantum yields are summarized in Table 1. Both OPV side chains 9b,c show similar and intense emission spectra with a maximum at 455 and 465 nm and a shoulder at 481 and 489 nm, respectively. They display a monoexponential decay with a fluorescence lifetime of \sim 1,3 ns and a fluorescence quantum yield of $\sim 70\%$.

The fluorescence spectrum of the polymer backbone **Pgal** (excitation at 550 nm) consists in a maximum at 611 nm and a shoulder at 665 nm, which is slightly more intense in toluene. The fluorescence quantum yield decreases, however, from 26% in THF to 15% in toluene. The fluorescence decays in THF and toluene can be analyzed globally from 610 until 665 nm as a sum of two exponentials with decay times of



Figure 6. Normalized absorbance and emission spectra of (a) 9b-c, (b) Pgal, (c) Pb, and (d) Pc.

Table 1. Fluorescence Lifetimes (τ) and Quantum Yields (Φ_f) of 9b, 9c, Pb, and Pc in Different Solvents

	solvent	$\lambda_{\rm ex} ({\rm nm})$	$\lambda_{\rm em} ({\rm nm})$	τ (ns)	$\Phi_{\rm f}$
9b	THF	375	480	1.28	0.67
9c	THF	375	490	1.32	0.72
Pgal	THF	550	610	0.15; 0.59	0.26
	toluene	550	610	0.10; 0.62	0.15
Pb	THF	375	600	0.04; ^{<i>a</i>} 0.73; 1.09	0.16
		550	600	0.03; ^{<i>a</i>} 0.47; 0.84	0.21
	THF/Et ₂ O	375	600	0.23; 0.84; 1.31	0.10
	, _	550	600	0.03; 0.89	0.17
Рс	THF	375	625	0.67	0.31
		550	610	$0.06;^a 0.66$	0.33
	THF/Et ₂ O	375	600	0.76, 1.02	0.16
	, _		700	0.76, 1.02	
		550	590	0.09; 0.79	0.16
			680	0.11; 1.01	
ac		1 4 + : 6 +			

^{*a*} Can be attributed to artifact or quenching processes.

 ~ 0.15 and ~ 0.6 ns. The ratio of the pre-exponential factors of the first and second decay time is much smaller than unity and does not depend on the wavelength (for a complete survey of all fluorescence data, see Supporting Information, Table S1). This suggests that in both solvents the emission originates from a single species. The nonexponential nature of the fluorescence decay is probably due to energy transfer to a nonfluorescent traps. If those findings are combined with the decrease in fluorescence quantum yield from THF to toluene, it can be concluded that light absorption in THF almost completely originates from isolated chromophores while in toluene about one-third of the light is absorbed by nonfluorescent, stacked (aggregated) chromophores (or aggregates with a very small fluorescence quantum yield), which is consistent with a helical conformation in which the chromophores lay on top of each other. The fraction of chromophores in the helical conformation will however be significantly larger than 1/3 as the helix absorbs at much longer wavelengths than 550 nm. Unfortunately, although

the polymer adopts two different conformations in THF and toluene (coil and helix), the nature of the emitting species—apart from being stacked or not—is hardly distinguishable in both conformations: the shape of the emission spectra, their λ_{em} and the fluorescence lifetime ($\tau \sim 0.6$ ns) are the same, only the quantum yield is significantly different.

If the fluorescence spectra of **Pb** and **Pc** are examined, the first conclusion that emerges, is that excitation of the OPV side chain results in an (almost) complete energy transfer from the OPV side chain to the PDTP backbone. The observed emission therefore arises from the polymer backbone, regardless whether the side chain or backbone is excited, and gives information on the macro- and/or supramolecular structure in which the polymer backbone is present.

The shape of the emission of **Pb** is again rather insensitive toward the solvent and excitation wavelength (375 or 550 nm) used and resembles the spectra of Pgal. The emissive decay (analyzed globally) is bi- or triexponential, from which one contribution (0.04 ns) can be attributed to artifacts or quenching. At both excitation wavelengths the main contribution shows a fluorescence lifetime of ~ 0.73 and ~ 0.84 ns in good (THF) and poor (THF/Et₂O) solvent, respectively. When excited at 375 nm, a third component of 1.09 ns (THF) and 1.31 ns (THF/Et₂O) is observed. Upon increasing the emission wavelength from 560 to 640 nm (THF/Et₂O) or from 600 to 665 nm (THF), the contribution of this component slightly increases. This component is probably due to aggregates of stacked chromophores. One should however note that over the wavelength range where fluorescence decays are analyzed, the fluorescence is mainly due to the component with a decay time of ~ 0.8 ns. This is again due to the fact that at the excitation wavelength used molecules in a coiled conformation are excited to a major extent (375 nm) or even nearly exclusively (550 nm). Moreover, the longliving contribution only becomes visible if the side chain is excited, which efficiently transfers its energy to the



Figure 7. Visualization of the structure of (left) Pb in a *cis*-configuration, (middle) Pc in a *cis*-configuration and (right) Pc in a planar, *trans*-configuration. The *cis*-configuration promotes a helical conformation, while the *trans*-configuration can result in lamellar stacks. The simulations were done with Hyperchem.



Figure 8. Schematic overview of the conformational changes in OPV-substituted PDTPs.

backbone. This indicates that energy transfer populates the stacked chromophores more efficiently than direct excitation of the backbone at 550 nm. The latter is confirmed by the overal drop in fluorescence quantum yield (in spite of the nearly complete excitation transfer) upon excitation of the side chains. It should also be noted that these emission data only indicates that the chromophores are stacked; they do not provide any information whether this stacking occurs intra- or intermolecularly. Therefore, it does not conflict with the results of the UV-vis and CD experiments.

The increase of the ~0.6 ns fluorescence decay time of **Pgal** to ~0.8 ns can be attributed to the decrease of motional freedom the DTP segments in **Pb** due to the increased size of the side chain. The increase of τ upon decreasing the solvent quality can be attributed to the decrease of the solvent polarity (THF versus THF/Et₂O), rather than it reflects a difference in macro- or supramolecular structure. For the same reason—the decrease of the solvent polarity, the emission spectra in THF/Et₂O are blue-shifted compared with neat THF. The decrease of the quantum yield in a poor solvent, finally, can be attributed to the fact that the possible aggregated chromophores in the helix have a very low fluorescence quantum yield. This suggests that, in a poor solvent a larger part of the light is absorbed by or transferred to aggregates.

The emission spectrum of **Pc** in THF again resembles the spectra of **Pgal** both upon excitation at 375 and 575 nm. The fluorescence decays of **Pc** obtained upon excitation at 375 nm in THF can be analyzed globally from 625 until 675 nm as a monoexponential decay ($\tau \sim 0.66$ ns), demonstrating that only one emitting type of chromophores is present; i.e., the backbone in its random coil conformation. Although upon excitation at 550 nm global analysis of the decays obtained between 610 and 665 nm requires a second decay time, the small value of this decay time (0.06 ns) suggests that this component has to be attributed to an

artifact or trapping by a nonfluorescent trap. The contribution of this component does moreover not depend upon the analysis wavelength and is very small. Furthermore, excitation at both 375 and 550 nm yields a similar fluorescence quantum yield (31-34%). All these data suggest that upon excitation at 375 or 550 nm only emission from isolated chromophores is obtained in THF. The fact that the fluorescence lifetime is somewhat higher than for **Pgal** can again be attributed to slower segmental motions due to the larger side chain.

In a poor solvent (THF/ Et_2O), two emission bands are observed with maximum at 596 and 688 nm, the latter being the most intense. While, considering the results obtained for Pb, the first band can be attributed to isolated chromophores, the second band—being absent in Pb—must be due to stacked chromophores. Upon excitation at 375 nm global analysis of the fluorescence decays from 600 until 700 nm yields a clear biexponential decay with decay times of 0.76 and 1.02 ns. Over this wavelength range the amplitude of the slowly decaying component increases from 12% to 30%. Analysis of the fluorescence obtained upon excitation at 550 nm reveals, except for a minor short-living contribution originating from artifacts or quenching, similar results. This confirms the hypothesis that the emission near 590 nm can be attributed to isolated chromophores in some residual coillike polymer chains, while the emission near 700 nm arises from stacked chromophores of aggregated polymer chains. One should note that, considering the absorption spectra of coiled and stacked chromophores, excitation at 500 nm will bias the excitation of coiled chromophores. The increase of the fluorescence lifetime of the polymer and the corresponding blue shift of the emission in its coil-like conformation from THF to THF/Et₂O (0.66 and 0.78 ns) can again be attributed to the decrease in polarity of the solvent. The quantum yield of fluorescence amounts 34% in THF, but is lower in the poor solvent mixture (16%), reflecting again the

low fluorescence quantum yield of the aggregated chromophores, already suggest for **Pb**. Since the fluorescence lifetime in a poor solvent is higher, the decrease in quantum yield cannot be attributed to quenching processes, but must instead originate from a lower oscillator strength of the emitting chromophore in a stacked configuration.

It can therefore be concluded that emission spectroscopy indicates that the same species, i.e. isolated chromophores, emit in **Pgal** and **Pc** in a good solvent. Slightly different emission properties are found for **Pgal** and **Pb** in poor solvents: in those cases, also (intramolecularly) aggregated chromophores are found. In **Pc** in poor solvent, however, significantly different emission properties, such as a distinct emission band with a corresponding longer fluorescence decay time, are measured, which can be attributed to (intermolecularly) aggregated chromophores. Furthermore, the amplitudes of the slower decaying component becomes larger at longer wavelengths (see Supporting Information, Table S1) Therefore, the fluorescence experiments confirm the proposed macromolecular and supramolecular behavior of the polymers.

Helical Conformation versus Aggregates. It is clear that Pa, Pb, and Pc show fundamentally different chiroptical properties, which results from the fact that completely different structures (random coils, helices, aggregates) are formed. In order to explain the origin of this totally different behavior in poor solvents, the conformation of Pb in a helical and Pc in a helical and planar conformation is visualized (Figure 7). This clearly reveals that a helical conformation is sterically allowed for Pb, but that the additional alkoxy substituents in Pc prevent this conformation, since steric repulsion between the alkoxy groups of adjacent monomeric units would force the substituent to adopt a twisted orientation. In this way, a helical backbone conformation, in which the pendant OPV side chains are stacked, is prevented. In contrast, a coplanar conformation poses no restrictions and is sterically allowed. Therefore, these calculations suggest that Pc does not adopt a helical conformation since this is sterically not allowed.

It can therefore be concluded that PDTPs substituted with OPVs equipped with a gallic acid moiety, adopt an unordered, coiled structure in a good solvent and show a tendency to fold into a helical conformation upon decreasing the solvent quality, unless this latter option is impeded by steric hindrance originating from α -substitution (Figure 8). It must be noticed that in both ways, the OPV side chains can be (chirally) organized by the polymer backbone. This has been visualized in Figure8.

Conclusion

In conclusion, the conformation and chiroptical properties of PDTPs substituted with OPV side chains which were equipped with a gallic acid derivative, have been investigated. It was found that the PDTP backbone adopts a helical conformation in a poor solvent, organizing the OPV side chains at the periphery, provided that the α -position of the OPV is not substituted. If the OPV moiety is equipped with chiral (alkyl) groups which are located sufficiently close to the polymer backbone, the space confinement result in a resolution of the mixture of isomeric

helical senses. In contrast, OPV–PDTPs of which the α -position of the OPV is substituted, cannot adopt a helical conformation due to steric restrictions; instead, the polymer strands planarize and stack in poor solvents. In both cases, the OPV side chains can be chirally aligned in poor solvents by the polymer backbone and they contribute significantly to the optical properties of the material.

Acknowledgment. We are grateful to the Katholieke Universiteit Leuven (GOA) and the Fund for Scientific Research (FWO-Vlaanderen) for financial support. L.P. is a doctoral fellow of IWT-Vlaanderen and G.K. is a postdoctoral fellow of the Fund for Scientific Research (FWO-Vlaanderen).

Supporting Information Available: Figures showing concentration dependent UV-vis and/or CD spectra of **Pa-c**, text giving an analysis of pre-exponential factors of the fluorescence decays of **9a,b** and **Pgal**, **Pb**, and **Pc** with a table of data, and figures showing NMR spectra of the new compounds. This material is available free of charge via the Internet at http:// pubs.acs.org.

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