Influence of the Substituent on the Chiroptical Properties of Poly(thieno[3,2-*b*]thiophene)s

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ABSTRACT: A series of chiral 3,6-substituted poly(thieno[3,2-*b*]thiophene)s (PTTs) were synthesized: 3,6-dialkoxy-substituted PTTs, 3,6-dialkylthio-substituted PTTs, and alternating copolymers of 3,6-dialkoxythieno-[3,2-*b*]thiophenes and 3,6-dialkylthieno[3,2-*b*]thiophenes. The polymers were prepared by a Stille-coupling reaction and their (chir)optical properties were investigated in solution as well as in film. The substituent appeared to play a decisive role in the polymer's macromolecular structure and supramolecular organization. The very small steric hindrance between the substituents and the polymer backbone of dialkoxy-substituted PTTs, in addition to the strong chalcogen−chalcogen attractions, allows these polymers to adopt a rigid rod-like conformation in good solvents. Upon transition to nonsolvents and film, the polymer strands chirally stack but no macroscopic order could be obtained. If the steric hindrance between adjacent monomer units is increased and the strength of the chalcogen−chalcogen attraction is decreased, as is the case in dialkylthio-substituted PTTs and the alternating copolymers, the polymers are present as random coils in solution. In films or in poor solvents, they planarize and stack and macroscopic order is present. Very large Cotton effects in both poor solvents and film were observed. In film, the CD spectra of some of the (semi-crystalline) polymers is a combination of "real" CD and other contributions.

Introduction

After the discovery of conductive polyacetylene in 1977,[1] interest in the field of conjugated polymers as new materials for electronic and optical devices surged.[2] Since then, conjugated polymers have been successfully employed as active layers in, for instance, polymeric light-emitting diodes (PLEDs),[3] polymeric field-effect transistors (PFETs),[4] and photovoltaic cells.[5] While all these properties mainly arise from the conjugated backbone, substitution of the polymer backbone is essential to obtain solubility. Moreover, the side chains often play a decisive role in the macromolecular structure and supramolecular organization, which are both determining factors for the polymer's properties. This is, for instance, well demonstrated in substituted polythiophenes.[6] Substitution with an alkyl substituent leads to steric hindrance between the methylene group of the substituent and the thiophene sulfur atom, resulting in twists between adjacent thiophene units within the polymer backbone. If too strong steric interactions between neighboring thiophene units are present, the polymer cannot adopt a planar conformation. This is the case in, for instance, poly(3,3′-dialkyl-2,2′-bithiophene),[7] which is characterized by poor conjugation lengths in both solution and film ($\lambda_{max} \sim 400$ nm). In head-to-tail coupled poly(3-alkylthiophene)s (HT-P3ATs),[8] moderate steric repulsions are present. These polymers adopt a random coil-like structure in solution ($\lambda_{max} \sim 460$ nm), but in nonsolvents or solid state, the backbone planarizes and the polymer strands aggregate ($\lambda_{max} \sim 560$ nm). Also regioregularity has a major influence on the physical properties. Because of the regioregular nature of HT-P3ATs, structural irregularities within the polymer backbone can be excluded, resulting in a high degree of packing order in the solid state. As a result, high charge carrier mobilities in PFETs were reported for regioregular P3ATs (μ up to 0.1 cm^2 V^{-1} s^{-1}).[4]

Also regioregular poly(3-alkoxythiophene)s (HT-P3AOTs) have been constructed.[9] In solution, these polymers already adopt a rather highly conjugated ($\lambda_{max} \sim 600$ nm), rigid rod-like conformation. This can be explained by the reduced steric hindrance between the substituent (O) and the polymer backbone (van der Waals radii: O ∼ 0.15 nm;[10] $CH_2 \sim 0.20$ nm)[6a,7c] and additional attractive S−O interactions.[11] Upon transition to the solid state, the polymer strands also aggregate ($\lambda_{max} \sim 630$ nm). However, in contrast to HT-P3ATs, which are semi-crystalline, HT-P3AOTs are amorphous materials and their solubility is lower.

In order to fabricate highly conjugated materials, the use of fused-ring heterocycles as building blocks for the polymer backbone is a powerful approach.[12] Semiconducting liquid-crystalline poly(2,5-bis(3-alkyl-thiophen-2-yl)thieno[3,2-*b*]thiophene)s have been prepared by McCulloch et al. and were demonstrated to possess a highly organized supramolecular structure.[13] As a consequence, high charge carrier mobilities ($\mu \sim 0.2-0.6$ cm^2 V^{-1} s^{-1}) were achieved in PFET devices. Also 3,6-dimethoxy-substituted poly(thieno[3,2-*b*]thiophene) (PTT) was already developed.[14] Unfortunately, this polymer lacks solubility. On the other hand, 3,6-dialkyl-substituted PTTs show an excellent solubility, but these polymers are poorly conjugated in both solution and the solid state ($\lambda_{max} \sim 360$ nm).[15] It is clear that the behavior of these different substituted PTTs is significantly influenced by the nature of the side-chain.

Here, we report the synthesis and characterization of three different PTTs as displayed in Chart 1: poly(3,6-dialkoxythieno-[3,2-*b*]thiophene)s (**P(O$^{(*)}$)**), poly(3,6-dialkylthiothieno[3,2-*b*]-thiophene)s (**P(S$^{(*)}$)**), and a series of alternating copolymers of 3,6-dialkoxythieno[3,2-*b*]thiophene with 3,6-dialkylthieno[3,2-*b*]thiophene (**P(O$^{(*)}$A$^{(*)}$)**). The nature of the substituents was varied in order to obtain PTTs which adopt a random coil-like structure in solution but can planarize and stack in poor solvents or films. In this way, well soluble PTTs can be obtained, which,

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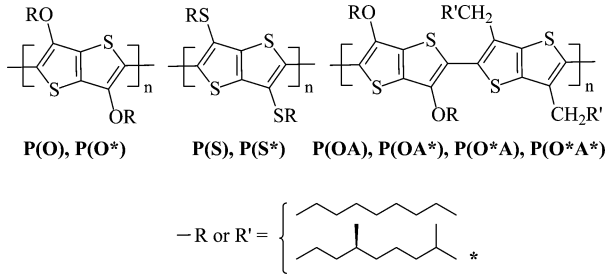
Chart 1. Structure of the Polymers



analogous to HT-P3ATs, can self-organize upon transition from solution to film.

In order to study the supramolecular organization by means of circular dichroism (CD) spectroscopy, also chiral polymers were prepared. CD spectroscopy has proven to be a highly sensitive tool for investigating the (chiral) supramolecular order in, for instance, alkyl-,[16] alkoxy-,[9b] aryl-substituted[17] polythiophenes, poly(phenylene vinylene)s[18] (PPVs), poly(phenylene ethynylene)s[19] (PPEs), poly(fluorene)s[20] (PFs), and poly(carbazole)s.[21]

Experimental Section

Reagents and Instrumentation. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried and purified by distillation.

Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) or chloroform as the eluent toward polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz spectrometer. UV−vis and CD spectra were recorded with a Varian Cary 400 and a JASCO 62 DS apparatus, respectively. Cyclic voltammetry was performed on a Princeton Applied Research PARSTAT 2273, equipped with a standard three-electrode configuration. A Ag/AgCl (3 M NaCl) electrode served as a reference electrode and a Pt wire and disk as the counter- and working electrode. The measurements were done in acetonitrile with Bu_4NBF_4 (0.1 M) as the supporting electrolyte under an argon atmosphere. Ferrocene was added before each run as an internal standard. The Fe(II/III) couple of ferrocene was observed at 0.45 V (scan rate = 50 mV/s). For the measurements, a polymer film was drop casted on the Pt disk working electrode. The DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus. The fluorescence measurements were done on a PTI Photon Technology International apparatus. The samples were excited near the absorption wavelength, and the quantum yields were determined using secondary methods.[22] The optical rotations were measured with a polAAr 20 apparatus; the solvent used and concentration (in g/100 mL) are given in parentheses. Films for UV−vis and CD experiments were prepared by spin coating from a chloroform-solution (1500 rpm, 20 s).

3,6-dibromothieno[3,2-*b*]thiophene (**1**),[23] (*S*)-(−)-3,7-dimethyloctanol (**5***),[16d] 3,6-dimethoxythieno[3,2-*b*]thiophene (**8**),[14] and (*S*)-(+)-1-bromo-3,7-dimethyloctane (**12***)[16d] were synthesized according to literature procedures.

Synthesis of 3,6-Dinon-1-ynylthieno[3,2-*b*]thiophene (3). To an argon-purged mixture of **1** (1.19 g, 4.00 mmol) and $Pd(PPh_3)_4$ (231 mg, 200 μmol) in dry piperidine (12 mL) at 70 °C was added via a syringe solution of 1-nonyne (**2**) (1.49 g, 12.0 mmol) in dry piperidine (2 mL). A solution of CuI (152 mg, 800 μmol) in dry piperidine (5 mL) was added via a syringe, and the reaction mixture was maintained at 80 °C for 24 h. After addition of hexanes, the solution was filtered to remove the precipitated salts. The organic layer was washed successively with 1 M hydrochloric acid, a saturated $NaHCO_3$ solution, and brine. Next, the organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Finally, the product was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as brown crystals. Yield: 627 mg (41%). mp: 34−35 °C. ^{1}H NMR ($CDCl_3$): δ = 7.39 (s, 2H), 2.44 (t, 4H), 1.63 (qu, 4H), 1.2−1.5 (m, 16H), 0.90 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 140.0, 129.6, 116.3, 93.2, 73.6, 31.9, 29.0, 28.8, 22.8, 19.6, 14.3. MS: m/z = 385 (M^+) (calcd, 385), 263 ($M^+ - C_9H_{14}$).

Synthesis of (4*S*,4′*S*)-(+)-3,6-Di(4,8-dimethylnon-1-ynyl)thieno-[3,2-*b*]thiophene (3*). Compound **3*** was obtained from **1** (1.19 g, 4.00 mmol) and (S)-(+)-4,8-dimethylnon-1-yne (**2***) (1.83 g, 12.0 mmol), following a similar procedure as described for **3**. The compound was isolated as a colorless oil. Yield: 788 mg (45%). = +4.82 deg dm^{-1} mol^{-1} L (c = 2.1 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 7.38 (s, 2H), 2.38 (m, 4H), 1.74 (m, 2H), 1.4−1.6 (m, 4H), 1.1−1.4 (m, 10H), 1.05 (d, 6H), 0.88 (d, 12H). ^{13}C NMR ($CDCl_3$): δ = 140.1, 129.4, 116.4, 92.0, 74.5, 39.2, 36.4, 32.8, 28.1, 26.9, 25.0, 22.8, 19.8. MS: m/z = 441 (M^+) (calcd, 441), 291 ($M^+ - C_{11}H_{18}$).

Synthesis of 3,6-Dinonylthieno[3,2-*b*]thiophene (4).[15] To a solution of **3** (1.34 g, 3.49 mmol) in ethyl acetate (30 mL) was added 10% Pd/C (270 mg). The mixture was stirred under H_2 atmosphere for 24 h (using a Parr apparatus). After reaction, the solution was filtered through celite and the solvent removed via rotary evaporation. The crude compound was purified by recrystallization from ethanol and isolated as white crystals. Yield: 755 mg (55%). mp: 50−51 °C. ^{1}H NMR ($CDCl_3$): δ = 6.95 (s, 2H), 2.70 (t, 4H), 1.74 (qu, 4H), 1.1−1.4 (m, 24H) 0.88 (t, 6H).

Synthesis of (4*S*,4′*S*)-(+)-3,6-Di(4,8-dimethylnonyl)thieno[3,2-*b*]thiophene (4*). Compound **4*** was obtained from **3*** (758 mg, 1.72 mmol), following a similar procedure as described for **4**. The crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as a colorless oil. Yield: 392 mg (51%). $[\alpha]_D^{20}$ = +1.89 deg dm^{-1} mol^{-1} L (c = 2.2 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 6.93 (s, 2H), 2.67 (m, 4H), 1.73 (m, 4H), 1.0−1.6 (m, 20H) 0.86 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 139.4, 135.6, 121.0, 39.5, 37.4, 37.0, 32.7, 30.3, 28.1, 26.4, 24.9, 22.9, 22.8, 19.8. MS: m/z = 449 (M^+) (calcd, 449).

Synthesis of (*S*)-(−)-3,7-Dimethyloctanal (6*).[24] To a solution of (*S*)-3,7-dimethyloctanol (**5***) (6.33 g, 40.0 mmol) in dichloromethane (400 mL), PCC (12.9 g, 60.0 mmol) was added in one portion at room temperature. Stirring was continued for 12 h under an argon atmosphere. After reaction, the precipitate was filtered off and the solvent was removed via rotary evaporation. The crude compound was purified by column chromatography (silica gel; eluent, dichloromethane) and isolated as a colorless oil. Yield: 4.05 g (65%). $[\alpha]_D^{20}$ = −0.80 deg dm^{-1} mol^{-1} L (c = 1.1 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 9.76 (t, J = 2.3 Hz, 1H), 2.39 (m, 1H), 2.22 (m, 1H), 2.06 (m, 1H), 1.54 (m, 1H), 1.1−1.4 (m, 6H), 0.96 (d, 3H), 0.87 (d, 6H).

Synthesis of (*S*)-(+)-1,1-Dichloro-4,8-dimethylnonene (7*). In portions sodium trichloroacetate (5.65 g, 30.5 mmol) was added to a stirred solution of trichloroacetic acid (4.98 g, 30.5 mmol) and **6*** (3.19 g, 20.4 mmol) in dry DMF (20 mL) at 25 °C. By addition, the internal temperature was kept below 35 °C. After addition was completed, the mixture was stirred at room temperature for 4 h with continuous evolution of CO_2. The solution was cooled to 5 °C, and acetic anhydride (3.78 mL, 40.0 mmol) was carefully added. Strong CO_2 evolution was observed. The mixture was allowed to warm to room temperature and stirred for an additional hour. The reaction mixture was diluted with acetic acid (18.7 mL) and cooled to 0 °C. Zinc powder (2.61 g, 40.0 mmol) was added to the solution in one portion. The solution was stirred for 1 h at 60 °C and subsequently cooled to room temperature. Water was added, and the compound was extracted with hexanes. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude compound was purified by column chromatography (silicagel; eluent, petroleum ether) and by distillation and isolated as a colorless oil. Yield: 2.00 g (44%). bp:110 °C/ 15 mmHg. $[\alpha]_D^{20}$ = +0.76 deg dm^{-1} mol^{-1} L

(c = 0.33 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 5.88 (m, 1H), 2.15 (m, 1H), 2.03 (m, 1H), 1.55 (m, 2H), 1.1−1.4 (m, 6H), 0.88 (m, 9H). ^{13}C NMR ($CDCl_3$): δ = 129.1, 120.2, 39.3, 37.0, 36.9, 32.9, 28.1, 24.9, 22.8, 22.8, 19.7. MS: m/z = 223 (M^+) (calcd, 223).

Synthesis of (*S*)-(+)-4,8-Dimethylnon-1-yne (2*). MeLi (23.2 mL, 37.1 mmol, 1.6 M in diethyl ether) was added via a syringe to a solution of **7*** (3.20 g, 14.3 mmol) in dry THF (20 mL) at −30 °C. After the addition was completed, the solution was allowed to warm to 0 °C slowly. The reaction was quenched with a saturated aqueous NH_4Cl solution and diluted with hexanes. The aqueous phase was extracted with hexanes. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed via rotary evaporation, leaving a colorless oil, which was used without further purification. Yield: 2.04 g (93%). $[\alpha]_D^{20}$ = +0.27 deg.dm^{-1}.mol^{-1}.L (c = 1.3 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 2.11 (m, 2H), 1.94 (t, J = 2.3 Hz, 1H), 1.65 (m, 1H), 1.53 (m, 1H), 1.1−1.5 (m, 6H), 0.98 (d, 3H), 0.87 (d, 6H). ^{13}C NMR ($CDCl_3$): δ = 83.6, 69.1, 39.2, 36.3, 32.5, 28.1, 25.9, 24.9, 22.8, 22.7, 19.5. MS: m/z = 152 (M^+) (calcd, 152).

Synthesis of 3,6-Dioctyloxythieno[3,2-*b*]thiophene (9). A solution of **8** (2.09 g, 10.5 mmol), octanol (**5**) (5.46 g, 42.0 mmol), and $NaHSO_4$ (125 mg, 1.05 mmol) in dry toluene (30 mL) was heated for 5 h while an azeotropic mixture of methanol and toluene was distilled off. After reaction, the solution was diluted with dichloromethane and washed with water and with a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Finally, the product was purified by recrystallization from acetonitrile and isolated as white crystals. Yield: 3.17 g (77%). mp: 91−92 °C. ^{1}H NMR ($CDCl_3$): δ = 6.23 (s, 2H), 4.05 (t, 4H), 1.81 (qu, 4H), 1.46 (m, 4H), 1.2−1.4 (m, 16H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 150.3, 128.7, 97.9, 70.7, 32.0, 29.5, 29.4, 29.3, 26.2, 22.8, 14.3. MS: m/z = 397 (M^+) (calcd, 397), 285 ($M^+ - C_8H_{16}$), 172 ($M^+ - C_{16}H_{32}$).

Synthesis of (3*S*,3′*S*)-(−)-3,6-Di(3,7-dimethyloctyloxy)thieno-[3,2-*b*]thiophene (9*). Compound **9*** was obtained from **8** (3.20 g, 16.0 mmol) and (*S*)-(−)-3,7-dimethyloctanol (**5***) (10.2 g, 64.1 mmol), following a similar procedure as described for **9**. The crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and by recrystallization from methanol and isolated as white crystals.

Yield: 2.5 g (35%). mp: 45−47 °C. $[\alpha]_D^{20}$ = −1.39 deg dm^{-1} mol^{-1} L (c = 1.9 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 6.23 (s, 2H), 4.07 (m, 4H), 1.85 (m, 2H), 1.5−1.7 (m, 6H), 1.1−1.4 (m, 12H), 0.94 (d, 6H), 0.87 (d, 12H). ^{13}C NMR ($CDCl_3$): δ = 150.3, 128.6, 97.8, 69.0, 39.4, 37.3, 36.1, 30.0, 28.1, 24.8, 22.8, 22.8, 19.8. MS: m/z = 453 (M^+) (calcd, 453), 313 ($M^+ - C_{10}H_{20}$), 172 ($M^+ - C_{20}H_{40}$).

Synthesis of (*S*)-(+)-3,7-Dimethyloctanethiol (10*). A solution of (*S*)-(+)-1-bromo-3,7-dimethyloctane (**12***) (8.85 g, 40.0 mmol) in THF (80 mL) was cooled to −10 °C, and hexamethyldisilathiane (8.57 g, 48.0 mmol) and tetrabutylammonium fluoride (44.0 mL, 44.0 mmol, 1.0 M in THF with 5% water) were added. The resulting reaction mixture was allowed to warm to room temperature and was stirred overnight. After reaction, the reaction mixture was diluted with dichloromethane and the organic layer was washed with a saturated aqueous solution of NH_4Cl. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Finally, the product was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as a colorless oil. Yield: 5.82 g (83%). $[\alpha]_D^{20}$ = +2.62 deg dm^{-1} mol^{-1} L (c = 2.1 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 2.54 (m, 2H), 1.55 (m, 4H), 1.0−1.4 (m, 7H), 0.87 (m, 9H). ^{13}C NMR ($CDCl_3$): δ = 41.6, 39.4, 37.0, 32.0, 28.1, 24.8, 22.8, 22.7, 22.6, 19.3. MS: m/z = 174 (M^+) (calcd, 174).

Synthesis of 3,6-Dioctylthiothieno[3,2-*b*]thiophene (11). Compound **11** was obtained from **8** (781 mg, 3.90 mmol) and octanethiol (**10**) (2.28 g, 15.6 mmol), following a similar procedure as described for **9**. The crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as white crystals. Yield: 1.13 g (68%). mp: 58−59 °C. ^{1}H NMR ($CDCl_3$): δ = 7.26 (s, 2H), 2.91 (t, 4H), 1.62 (qu, 4H), 1.40 (m, 4H), 1.26 (m, 16H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 141.3, 127.1, 125.1, 34.7, 31.9, 29.8, 29.3, 29.2, 28.7, 22.8, 14.2. MS: m/z = 429 (M^+) (calcd, 429).

Synthesis of (3*S*,3′*S*)-(+)-3,6-Di(3,7-dimethyloctylthio)thieno-[3,2-*b*]thiophene (11*). Compound **11*** was obtained from **8** (601 mg, 3.00 mmol) and (*S*)-(+)-3,7-dimethyloctanethiol (**10***) (2.27 g, 13.0 mmol), following a similar procedure as described for **9**. The crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as a colorless oil. Yield: 1.08 g (74%). $[\alpha]_D^{20}$ = +14.8 deg dm^{-1} mol^{-1} L (c = 1.2 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 7.25 (s, 2H), 2.92 (m, 4H), 1.4−1.7 (m, 8H), 1.0−1.3 (m, 12H), 0.86 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 141.2, 126.9, 125.1, 39.3, 37.0, 36.9, 32.6, 32.1, 28.1, 24.8, 22.8, 22.8, 19.5. MS: m/z = 485 (M^+) (calcd, 485).

Synthesis of 2,5-Bromo-3,6-dinonylthieno[3,2-*b*]thiophene (13). A solution of **4** (589 mg, 1.50 mmol) in dry THF (20 mL) was shielded from light and brought under an argon atmosphere. At −78 °C, *N*-bromosuccinimide (570 mg, 3.20 mmol) was added and the reaction solution was allowed to warm to room temperature slowly and stirred overnight. After dilution of the solution with diethyl ether, the organic layer was thoroughly washed with water and dried over anhydrous $MgSO_4$. The solvents were removed in vacuo, and the crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as white crystals. Yield: 803 mg (97%). mp: 50−51 °C. ^{1}H NMR ($CDCl_3$): δ = 2.66 (t, 4H), 1.65 (qu, 4H), 1.1−1.4 (m, 24H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 136.3, 134.5, 109.6, 32.0, 29.6, 29.5, 29.1, 28.2, 22.8, 14.3. MS: m/z = 551 (M^+) (calcd, 551), 470 (M^+ − Br).

Synthesis of (4*S*,4′*S*)-(+)-2,5-Dibromo-3,6-di(4,8-dimethylnonyl)thieno[3,2-*b*]thiophene (13*). Compound **13*** was obtained from **4*** (340 mg, 758 μmol), following a similar procedure as described for **13**. The product was isolated as a colorless oil. Yield: 385 mg (84%). $[\alpha]_D^{20}$ = +2.25 deg dm^{-1} mol^{-1} L (c = 2.1 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 2.64 (t, 4H), 1.65 (m, 4H), 1.0−1.6 (m, 20H), 0.85 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 136.2, 134.5, 109.6, 39.4, 37.3, 36.7, 32.6, 29.4, 28.1, 25.7, 24.9, 22.9, 22.8, 19.7. MS: m/z = 607 (M^+) (calcd, 607), 526 (M^+ − Br).

Synthesis of 2,5-Dibromo-3,6-dioctyloxythieno[3,2-*b*]thiophene (14). Compound **14** was obtained from **9** (594 mg, 1.50 mmol), following a similar procedure as described for **13**. The product was isolated as white crystals. Yield: 729 mg (88%). mp: 47−48 °C. ^{1}H NMR ($CDCl_3$): δ = 4.21 (t, 4H), 1.76 (qu, 4H), 1.48 (m, 4H), 1.2−1.4 (m, 16H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 147.6, 126.7, 95.7, 73.0, 31.9, 30.0, 29.3, 25.9, 22.8, 14.3. MS: m/z = 555 (M^+) (calcd, 554), 443 ($M^+ - C_8H_{16}$), 330 ($M^+ - C_{16}H_{32}$).

Synthesis of (3*S*,3′*S*)-(+)-2,5-Dibromo-3,6-di(3,7-dimethyloctyloxy)thieno[3,2-*b*]thiophene (14*). Compound **14*** was obtained from **9*** (511 mg, 1.13 mmol), following a similar procedure as described for **13**. The product was isolated as a colorless oil. Yield: 603 mg (87%). $[\alpha]_D^{20}$ = +1.82 deg dm^{-1} mol^{-1} L (c = 1.5 in dichloromethane). ^{1}H NMR ($CDCl_3$): δ = 4.25 (m, 4H), 1.77 (m, 4H), 1.54 (m, 4H), 1.1−1.4 (m, 12H), 0.95 (d, 6H), 0.87 (d, 12H). ^{13}C NMR ($CDCl_3$): δ = 147.6, 126.7, 95.6, 71.3, 39.3, 37.3, 37.0, 29.7, 28.1, 24.8, 22.8, 22.8, 19.7. MS: m/z = 610 (M^+) (calcd, 611), 530 (M^+ − Br), 471 ($M^+ - C_{10}H_{20}$), 391 ($M^+ - C_{10}H_{20}Br$), 330 ($M^+ - C_{20}H_{40}$).

Synthesis of 2,5-Dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (15). Compound **15** was obtained from **11** (858 mg, 2.00 mmol), following a similar procedure as described for **13**. The product was isolated as white crystals. Yield: 1.01 g (86%). mp: 45−46 °C. ^{1}H NMR ($CDCl_3$): δ = 2.87 (t, 4H), 1.55 (qu, 4H), 1.39 (m, 4H), 1.25 (m, 16H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 139.5, 125.7, 119.3, 34.8, 31.9, 30.1, 29.3, 29.2, 28.6, 22.8, 14.3. MS: m/z = 587 (M^+) (calcd, 587).

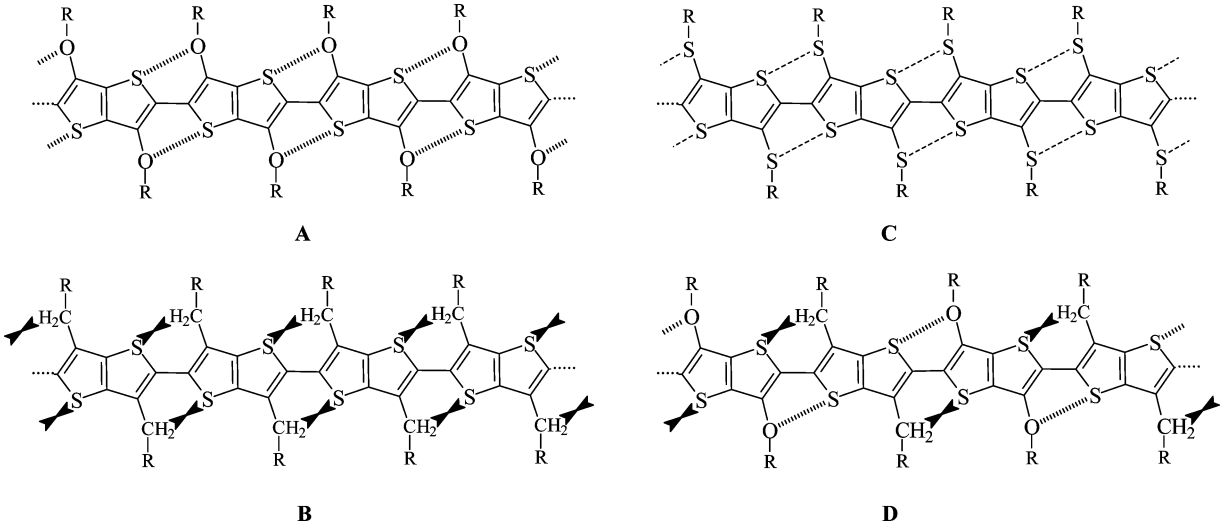


Figure 1. Attractions versus repulsions in poly(thieno[3,2-*b*]thiophene)s.

Synthesis of (3*S*,3′*S*)-(+)-2,5-Dibromo-3,6-di(3,7-dimethyloctylthio)thieno[3,2-*b*]thiophene (15*). Compound **15*** was obtained from **11*** (485 mg, 1.00 mmol), following a similar procedure as described for **13**. The product was isolated as a colorless oil. Yield: 584 mg (91%). $[\alpha]_D^{20} = +13.4$ deg dm^{-1} mol^{-1} L ($c = 1.6$ in dichloromethane). ^{1}H NMR ($CDCl_3$): $\delta = 2.90$ (m, 4H), 1.3−1.7 (m, 8H), 1.0−1.3 (m, 12H), 0.85 (m, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 139.4, 125.6, 119.1, 39.3, 37.1, 36.9, 32.6, 31.9, 28.1, 24.7, 22.8, 22.8, 19.4$. MS: $m/z = 642$ (M^+) (calcd, 643), 563 ($M^+ - Br$), 483 ($M^+ - Br_2$), 309 ($M^+ - C_{10}H_{21}SBr_2$).

Synthesis of 2,5-Di(trimethyltin)-3,6-dioctyloxythieno[3,2-*b*]-thiophene (16). At 0 °C and under an argon atmosphere, *t*-BuLi (3.50 mL, 5.25 mmol, 1.5 M in pentane) was cannulated to a solution of **9** (992 mg, 2.50 mmol) in dry diethyl ether (100 mL). The reaction was stirred for 1 h at room temperature, and a solution of Me_3SnCl (1.15 g, 5.75 mmol) in dry diethyl ether (5 mL) was added dropwise via a syringe. After stirring overnight at room temperature, the solution was concentrated in vacuo. The crude compound was redissolved in *n*-hexane and the solution was filtered to remove the precipitated salts. The solvent was removed via rotary evaporation, and the crude compound was purified by recrystallization from acetonitrile and isolated as white crystals. Yield: 1.51 g (84%). mp: 67−68 °C. ^{1}H NMR ($CDCl_3$): $\delta = 4.19$ (t, 4H), 1.74 (qu, 4H), 1.2−1.5 (m, 20H), 0.89 (t, 6H), 0.36 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 154.7, 136.2, 117.5, 72.0, 32.0, 30.2, 29.5, 29.4, 26.1, 22.8, 14.3, -8.1$. MS: $m/z = 722$ (M^+) (calcd, 722), 559 ($M^+ - C_3H_8Sn$), 397 ($M^+ - C_6H_{16}Sn_2$), 285 ($M^+ - C_{14}H_{32}Sn_2$), 172 ($M^+ - C_{22}H_{48}Sn_2$).

Synthesis of (3*S*,3′*S*)-(+)-2,5-Di(trimethyltin)-3,6-di(3,7-dimethyloctyloxy)thieno[3,2-*b*]thiophene (16*). Compound **16*** was obtained from **9*** (679 mg, 1.50 mmol), following a similar procedure as described for **16**. After removal of the salts, the crude compound was isolated as a lila, viscous oil which was used without further purification. Yield: 1.16 g (99%). $[\alpha]_D^{20} = +0.83$ deg dm^{-1} mol^{-1} L ($c = 2.1$ in dichloromethane). ^{1}H NMR ($CDCl_3$): $\delta = 4.22$ (t, 4H), 1.6−1.9 (m, 4H), 1.4−1.6 (m, 4H), 1.0−1.4 (m, 12H), 0.95 (d, 6H), 0.87 (d, 12H), 0.36 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 154.7, 136.2, 117.4, 70.3, 39.4, 37.4, 37.3, 29.8, 28.1, 24.9, 22.9, 22.8, 19.9, -8.1$. MS: $m/z = 778$ (M^+) (calcd, 778), 615 ($M^+ - C_3H_8Sn$), 453 ($M^+ - C_6H_{16}Sn_2$).

Synthesis of 2,5-Di(trimethyltin)-3,6-dioctylthiothieno[3,2-*b*]-thiophene (17). Compound **17** was obtained from **11** (429 mg, 1.00 mmol), following a similar procedure as described for **16**. After removal of the salts, the crude compound was isolated as white crystals which were used without further purification. Yield: 747 mg (99%). mp: 42−43 °C. ^{1}H NMR ($CDCl_3$): $\delta = 2.86$ (t, 4H), 1.59 (qu, 4H), 1.1−1.5 (m, 20H), 0.87 (t, 6H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 149.9, 146.9, 131.1, 35.6, 32.0, 30.2, 29.3, 29.2, 29.0, 22.8, 14.2, -7.2$. MS: $m/z = 754$ (M^+) (calcd, 754), 430 ($M^+ - C_6H_{16}Sn_2$).

Synthesis of (3*S*,3′*S*)-(+)-2,5-Di(trimethyltin)-3,6-di(3,7-dim-ethyloctylthio)thieno[3,2-*b*]thiophene (17*). Compound **17*** was obtained from **11*** (485 mg, 1.00 mmol), following a similar procedure as described for **16**. After removal of the salts, the crude compound was isolated as a green, viscous oil which was used without further purification. Yield: 802 mg (99%). $[\alpha]_D^{20} = +6.91$ deg dm^{-1} mol^{-1} L ($c = 1.9$ in dichloromethane). ^{1}H NMR ($CDCl_3$): $\delta = 2.87$ (m, 4H), 1.4−1.7 (m, 8H), 1.0−1.4 (m, 12H), 0.85 (m, 18H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 149.8, 146.9, 131.1, 39.4, 37.2, 36.9, 33.5, 32.4, 28.1, 24.7, 22.9, 22.8, 19.5, -7.2$. MS: $m/z = 811$ (M^+) (calcd, 811).

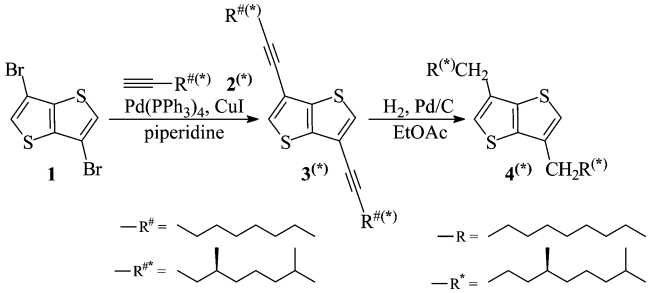
Synthesis of 2,5-Diiodo-3,6-dioctylthiothieno[3,2-*b*]thiophene (18). A solution of **11** (429 mg, 1.00 mmol) in dry DMF (20 mL) was shielded from light and brought under an argon atmosphere. *N*-Iodosuccinimide (900 mg, 4.00 mmol) was added, and the reaction solution was stirred overnight at 70 °C. After addition of hexanes, the organic layer was thoroughly washed with water and with a saturated $Na_2S_2O_3$ solution. After drying over anhydrous $MgSO_4$, the solvents were removed in vacuo. The crude compound was purified by column chromatography (silica gel; eluent, petroleum ether) and isolated as white crystals. Yield: 411 mg (60%). mp: 50−51 °C. ^{1}H NMR ($CDCl_3$): $\delta = 2.87$ (t, 4H), 1.55 (qu, 4H), 1.40 (m, 4H), 1.25 (m, 16H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 143.8, 130.7, 87.9, 35.2, 31.9, 30.1, 29.3, 29.2, 28.6, 22.8, 14.3$. MS: $m/z = 681$ (M^+) (calcd, 681), 554 ($M^+ - I$).

Synthesis of the Polymers. A general procedure is as follows: A solution of distannylated monomer (300 μmol), dibrominated monomer (300 μmol), $Pd(PPh_3)_4$ (17.4 mg, 15.0 μmol) in dry toluene (9 mL), and dry DMF (9 mL) was purged with argon for 0.5 h and then gently refluxed for 24 h. The polymer was concentrated and poured into methanol after cooling down. The polymer was filtered off and was further purified by Soxhlet extractions using successively acetone, *n*-hexane, and chloroform. The chloroform-soluble fraction (or *n*-hexane-soluble fraction in case of entire solubility in *n*-hexane) was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

Results and Discussion

The aim of the work is the development of poly(thieno[3,2-*b*]thiophene)s (PTTs) which combine solubility, macroscopic order, high conjugation lengths, and strong chiral expression. As already mentioned in the introduction, the choice of the substituent can play a crucial role for this purpose. Figure 1 displays a comparison between PTTs, substituted with different substituents. In dialkoxy-substituted PTTs (Figure 1A), no, or

Scheme 1. Synthesis of Alkyl-Substituted Thieno[3,2-*b*]thiophenes



very small, steric interactions between the substituent (O) and the polymer backbone, together with very strong S−O interactions, are present. Therefore, these polymers adopt a rigid rodlike structure in solution, which can further aggregate upon transition to the solid state. Their very strong tendency to aggregate limits their solubility. In fact, the already prepared *dimethoxy*-substituted PTT is insoluble in any organic solvent.[14] On the other hand, in dialkyl-substituted PTTs (Figure 1B) a lot of steric hindrance between adjacent monomer units is present, which complicate (and even exclude) the formation of planar structures.[15] Hence, these polymers adopt a poorly conjugated ($\lambda_{max} \sim 360$ nm) random coil-like structure in both solution and film. Therefore, it is clear that a proper choice of the substituent plays a crucial role in order to fabricate PTTs that are present as random coils in solution and as self-organized ordered, conjugated structures in the solid state. This can be achieved by carefully adjusting the ratio between steric hindrance and attractive chalcogen−chalcogen (for instance S−O) interactions. A first approach is the development of dialkylthio-substituted PTTs (Figure 1C). The van der Waals radius of a sulfur atom (∼0.18 nm) is intermediate between that of oxygen (∼0.15 nm) and methylene (∼0.20 nm).[6a,7c,10] Consequently, moderate steric hindrance can be expected, together with moderate S−S interactions.[11b] Another approach is the construction of alternating copolymers between dialkoxy- and dialkyl-substituted TTs in which both moderate repulsions and attractions are present (Figure 1D). In both ways, these polymers can possibly be present as random coils in solution, which, like HT-P3ATs, can planarize and aggregate upon transition to the solid state. Hence, these polymers could exhibit macroscopic order as well (semicrystalline polymers).

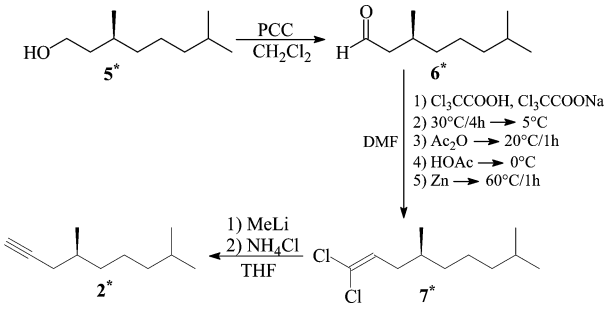
In order to be able to investigate the chiroptical properties of the polymers, chiral polymers were also prepared. Throughout this manuscript, the asterisk ∗ denotes the use of a chiral side chain.

Monomer Synthesis. The synthesis of achiral and chiral alkyl-substituted thieno[3,2-*b*]thiophenes (**4**$^{(*)}$) is depicted in Scheme 1. **4**$^{(*)}$ was prepared by a Sonogashira reaction between **1** and the alkyne **2**$^{(*)}$, followed by hydrogenation. It is worthwhile to note that in terms of yield, it was observed that piperidine appeared to be a better choice than triethylamine.

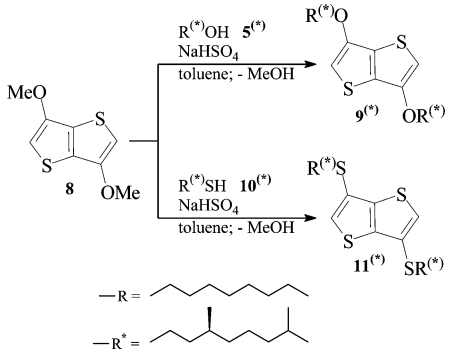
The chiral alkyne **2*** was prepared as described in Scheme 2. Oxidation of **5*** was accomplished using PCC. Next, the vinyl dichloride was prepared in a three-step, one-pot reaction involving the formation of trichlorocarbinol by treatment of the aldehyde with trichloroacetic acid and sodium trichloroacetate followed by in situ protection and elimination reactions.[25] Finally, the chiral alkyne **2*** was obtained in a reaction of **7*** with MeLi.

The alkoxy- and thioalkyl-substituted thieno[3,2-*b*]thiophenes **9**$^{(*)}$ and **11**$^{(*)}$ were obtained via a transetherification reaction from **8**, as outlined in Scheme 3.[26] The synthesis of the chiral

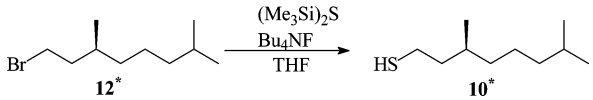
Scheme 2. Synthesis of (*S*)-(+)-4,8-Dimethylnon-1-yne



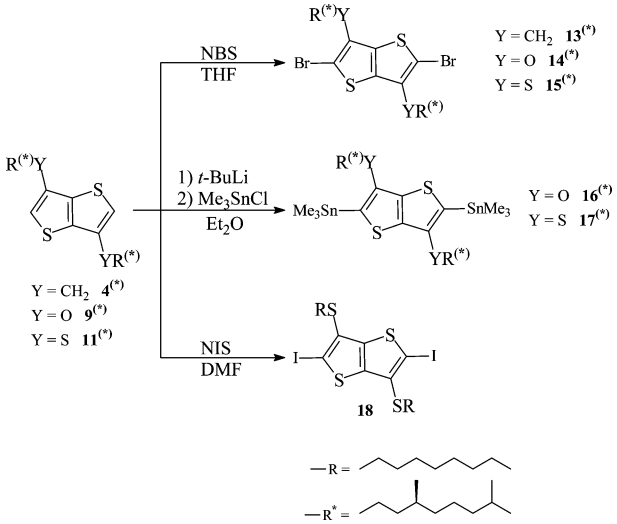
Scheme 3. Synthesis of Alkoxy- and Alkylthio-Substituted Thieno[3,2-*b*]thiophenes



Scheme 4. Synthesis of (*S*)-(+)-3,7-Dimethyloctanethiol



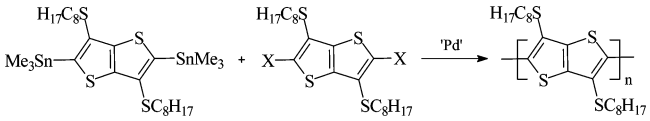
Scheme 5. Synthesis of the Monomers



thiol **10*** is displayed in Scheme 4 and involves the reaction of **12*** with in situ generated tetrabutylammonium trimethylsilylthiolate (Me_3SiS^- Bu_4N^+) followed by aqueous workup.[27]

The synthesis of the monomers is depicted in Scheme 5. Bromination of **4**$^{(*)}$, **9**$^{(*)}$, and **11**$^{(*)}$ was accomplished using *N*-bromosuccinimide (NBS), while iodination of **11** was performed using *N*-iodosuccinimide (NIS). The distannylated monomers **16**$^{(*)}$ and **17**$^{(*)}$ were prepared by dilithiation of **9**$^{(*)}$ and **11**$^{(*)}$, respectively, using *t*-BuLi, followed by quenching with Me_3SnCl. The achiral tin compounds **16** and **17** are solids and could be efficiently purified by recrystallization when necessary; the chiral tin compounds **16*** and **17*** are oils which could not be purified by column chromatography (since destan-

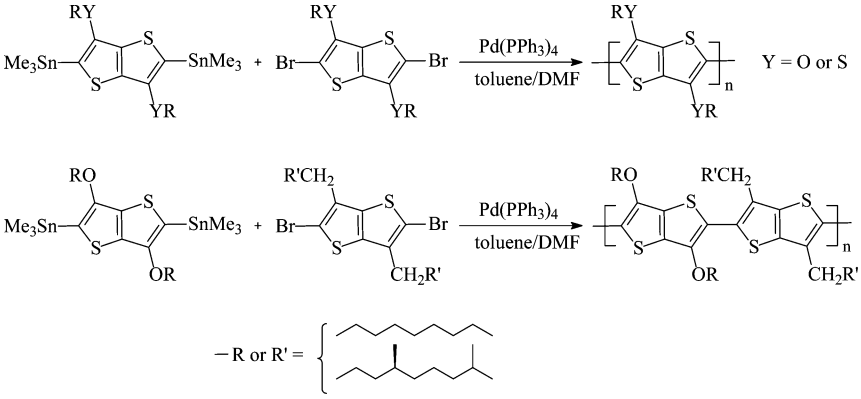
Table 1. Yields, Molecular Weights, and Polydispersities of the Test Polymerizations



entry	X	catalyst, ligand	solvent	*T*/°C	*t*/h	yield[a]/%	$\bar{M}_n$[b]/g mol^{-1}	PDI[b]
1	Br	$Pd(PPh_3)_4$ + CuO	toluene/DMF	100	24	50	5900	1.5
2	Br	$Pd(PPh_3)_4$	toluene/DMF	100	24	55	5700	1.5
3	Br	Pd_2dba_3, $AsPh_3$	THF/DMF	60	48	2	3300	1.3
4	I	$Pd(PPh_3)_4$ + CuO	toluene/DMF	60	60	6	3800	1.2
5	I	$Pd(PPh_3)_4$ + CuO	toluene/DMF	100	24	7	3700	1.3
6	I	$Pd(PPh_3)_4$	toluene/DMF	100	60	16	3500	1.2
7	I	Pd_2dba_3, $AsPh_3$	THF/DMF	60	60	38	4600	1.4

[a] Of the chloroform-soluble fraction. [b] Determined by GPC in chloroform toward polystyrene standards.

Scheme 6. Synthesis of the Polymers



nylation occurs). Fortunately, **16*** and **17*** were sufficiently pure after reaction to be used without further purification.

Polymer Synthesis. All polymers were synthesized by a polycondensation of distannylated and dihalogenated monomers using a Stille-coupling. The polymerization conditions were optimized and are displayed in Table 1. Concerning the halogen used, it is obvious that the use of diiodinated compounds results in much lower yields and molecular weights. Next, two different protocols were employed (entry 2 and 3). Finally, the effect of CuO in the polymerization was investigated.[28] As can be concluded from entry 1 and 2, the use of CuO in the polymerization had only a minor effect on the molecular weight and yield. In order to avoid contamination of CuO, CuO was not chosen in all other polymerizations. Therefore, the conditions of entry 2 were employed as the optimized conditions for all other Stille-polymerizations in this manuscript. The synthesis of all polymers is summarized in Scheme 6.

For the alternating copolymers, special care was taken to use electron-rich distannylated monomers in combination with electron-deficient dihalides, in order to achieve high molecular-weight polymers.[29]

After polymerization, all polymers were washed successively with acetone and *n*-hexane using a Soxhlet apparatus to remove byproducts and oligomers. Finally, the polymers were extracted with chloroform, precipitated into methanol, and dried. The chiral alternating copolymers (**P(OA*)**, **P(O*A)** and **P(O*A*)**), however, are soluble in *n*-hexane, and therefore, the *n*-hexane fraction of these polymers was precipitated into methanol and dried. The structure of all polymers was confirmed by ^{1}H NMR spectroscopy (see Supporting Information). No structural defects are present, which confirms the regular structure.

Because of the very poor solubility of achiral **P(O)**, the physical properties of this polymer are not withdrawn in this manuscript. All other polymers are well soluble in chloroform and THF, although the solubility of **P(O*)** was clearly lower than that of the other polymers. For the chiral alkylthio-substituted PTTs, both the chloroform-soluble fraction (indicated as **P(S*)**) and *n*-hexane-soluble fraction (indicated as **P(S*)_hex**) were taken into account in the determination of the physical properties.

Yield, GPC, and DSC Analysis. The yields and molecular weights of all polymers are listed in Table 2. High polymer yields (∼50−90%) were obtained for the Stille-polymerizations. The molecular weights were determined by GPC in chloroform or THF toward polystyrene standards. The molecular weight of **P(O*)** is remarkable higher than that of the other polymers. This might be explained by the fact that **P(O*)**, as will be shown, adopts a highly planar, rigid rod-like conformation, while all other polymers are present as random coils in good solvents. It has been shown that GPC typically overestimates the molecular weight of rigid polymers.[30]

Except for **P(O*)**, all polymers are semi-crystalline as indicated by presence of clear melting and crystallization peaks in DSC. This points to a highly ordered structure of these polymers in the solid state. On the other hand, **P(O*)** is an amorphous polymer with a glass transition around 127 °C. All polymers did not degrade below 250 °C.

Electrochemistry. The potential of the peak anodic current (E_{pa}) and peak cathodic current (E_{pc}) of the films, drop casted from a chloroform solution onto the Pt working electrode, were measured using cyclic voltammetry. It is worthwhile to note that the peaks shift to lower potentials after the first scan cycle through the oxidation process, indicating the formation of a more conjugated system. After the second scan, the position and also the shape of the voltammograms remained unchanged. Therefore, E_{pa} and E_{pc} were determined from the second scan. The oxidation processes of all polymers were quasi-reversible. The alternating copolymers have a half-wave potential ($E_{1/2} = (E_{pa}$

Table 2. Yield, Molecular Weight, Polydispersity, Degree of Polymerization, and Thermal and Electrochemical Data of the Polymers

polymer	yield[a]/%	$\bar{M}_n$[b]/g mol^{-1}	PDI[b]	DP[c]	T_g[d]/°C	T_m[d]/°C	T_c[e]/°C	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V
P(O*)	60	27 700[h]	2.2[h]	62	127	*i*	*i*	0.50	0.40	0.45
P(S)	55	5 700[h]	1.5[h]	13	*i*	206	191	1.18	0.84	1.01
P(S*)	15[f]	9 000	1.3	19	*i*	162	140	1.10	0.80	0.95
P(S*)_hex	36[g]	5 400	1.3	11	*i*	121	101	1.40	1.05	1.23
P(OA)	74	18 700	2.5	48	*i*	210	192	0.88	0.55	0.72
P(OA*)	88[g]	13 400	2.5	32	*i*	181	179	0.91	0.55	0.73
P(O*A)	71[g]	8 200	1.5	20	*i*	154	151	0.92	0.59	0.76
P(O*A*)	72[g]	8 000	1.5	18	*i*	148	128	0.90	0.54	0.72

[a] Of the chloroform-soluble fraction. [b] Determined by GPC in THF toward polystyrene standards. [c] Degree of polymerization (number of thieno[3,2-*b*]thiophene repeating units in the polymer). [d] Determined by DSC at a heating rate of 20 °C/min. [e] Determined by DSC at a cooling rate of 20 °C/min. [f] The total yield of **P(S*)** and **P(S*)_hex** is 51%. [g] Of the *n*-hexane-soluble fraction. [h] Determined by GPC in chloroform toward polystyrene standards. [i] Not detected.

Table 3. Optical Data of the Polymers in Solution and Film

	λ_{max} in solution/nm			λ_{max} in film/nm			
	$CHCl_3$		$CHCl_3/CH_3OH$ ($^1/_9$)				
polymer	neutral	oxidized[a]	neutral	neutral	oxidized[b]	$\Delta\lambda$[c]/nm	E_g[d]/eV
P(O*)	536	785, 1730	511	544	822, 1508	8	1.85
P(S)	447	824, >2000	565	600	904, >2000	153	1.74
P(S*)	449	831, >2000	574	596	840, >2000	147	1.77
P(S*)_hex	442	798, >2000	535	563	816, >2000	121	1.80
P(OA)	424	839, >2000	557	544	831, >2000	120	1.91
P(OA*)	425	811, >2000	523	515	827, >2000	90	1.94
P(O*A)	422	811, >2000	510	519	827, >2000	97	1.96
P(O*A*)	422	811, 1820	508	516	816, >2000	94	2.00

[a] By addition of a concentrated $NOBF_4$-solution (in chloroform). [b] By exposure to $NOBF_4$ (in acetonitrile). [c] Bathochromic shift upon transition from chloroform-solution to film. [d] Optical band gap, calculated from the onset of the absorption band in film.

$+ E_{pc})/2$) of ~0.75 V, which is lower than $E_{1/2}$ of dialkyl-substituted PTTs ($E_{1/2} = 1.00$ V).[15] For **P(O*)**, $E_{1/2} = 0.45$ V. It is clear that more electron-donating alkoxy substituents lower $E_{1/2}$. As a consequence, these polymers can easily be oxidized with, for instance, iodine. Alkylthio-substituted PTTs show a relatively high $E_{1/2}$ value. This is consistent with the fact that these materials could not be oxidized with iodine in the film (see below). Finally, the onsets of the oxidation waves were 0.20, 0.85, and 0.60 V for dialkoxy PTTs, dialkylthio PTTs, and the alternating copolymers, respectively. From these values, the HOMO levels of the polymers can be calculated to be −4.63, −5.28, and −5.03 eV.[31]

Chiroptical Properties in Solution. The absorption data are summarized in Table 3. Representative spectra in good and poor solvent are shown in Figure 2A,B. Because of the strong intramolecular S−O attractions, **P(O*)** adopts a planar, highly conjugated structure in chloroform ($\lambda_{max} = 536$ nm). Upon addition of a nonsolvent (methanol), no red-shift is observed (a blue-shift of ~20 nm occurs) but a clear vibronic fine-structure arises. Moreover, as can been observed in the CD spectrum (Figure 2C), a clear bisignate Cotton effect in the $\pi-\pi^*$ transition of the backbone appears. The presence of a bisignate Cotton effect is indicative of chiral exciton coupling of chirally stacked rigid, coplanar polymer strands.[32] This chiral exciton coupling is an *inter*molecular effect. These findings are consistent with (chiral) aggregation of rigid rods upon addition of nonsolvent. The anisotropy factor (defined as $g_{abs} = \Delta\epsilon/\epsilon$) was on the order of 5×10^{-3} for **P(O*)**.

These results are in contrast to all other polymers (**P(S$^{(*)}$)**, **P(O$^{(*)}$A$^{(*)}$)**), in which more steric hindrance within the polymer backbone is present. In a good solvent, these polymers are present as poorly conjugated, random coils (λ_{max} ~ 420−450 nm), which planarize and stack upon addition of a nonsolvent, resulting in a significant red-shift (~90−120 nm) and occurrence of fine-structure in the UV−vis spectra. Compared to HT-P3ATs (~65 nm), these red-shifts are very high. CD reveals the occurrence of clear bisignate Cotton effects in all these polymers, which is again due to chiral exciton coupling. A very high g_{abs}-value of more than 2×10^{-2} was obtained for **P(S*)**, which decreases to 2×10^{-3} for **P(S*)_hex**. This implies that the chiral packing is more effective in the higher molecular-weight **P(S*)** than in its lower molecular-weight counterpart **P(S*)_hex**. Interestingly, the Cotton effects of the chiral alternating copolymers are by far not equal in intensity. Their g_{abs}-values vary between 1×10^{-3} (**P(OA*)**, **P(O*A*)**) and 8×10^{-3} (**P(O*A)**). A difference in CD intensity of alternating copolymers in which one or two of the monomers is chiral was also observed in chiral poly(phenylene-*alt*-bithiophene)s[33] and can be explained by the fact that all three chiral alternating copolymers adopt (slightly) different supramolecular structures, each with corresponding different CD spectra. It is important to emphasize that the (chiral) supramolecular order, indicated by the presence of bisignate Cotton effects, relates to *meso*scale order and does, therefore, not conflict with the presence/absence of *macro*scale order as observed by DSC (semi-crystalline versus amorphous).

Fluorescence. Solution emission data for the polymers are summarized in Table 4. All spectra were recorded in chloroform. All polymers show strong emission around 540−590 nm. Fluorescence is an interesting tool to investigate the rigidity of the polymer backbone. Full width at half-maxima (fwhm) for the dialkylthio-substituted PTTs and for the alternating copolymers are on the order of 2600−3100 cm^{-1}, which are typical values for random coil-like structures.[34] The fwhm of **P(O*)**, however, is ~1700 cm^{-1}, which points at a much more rigid polymer backbone.[35] Also the Stokes shifts confirm our hypothesis: **P(O*)** has a reduced Stokes shift (~1700 cm^{-1}), in contrast to the other polymers which have larger Stokes shifts (~4900−5300 cm^{-1}), indicative of a flexible, random coil-like conformation in solution.[34,36] The quantum yields of the polymers amount to 23−43%. It has been shown for polyalkylthiophenes that the quantum yield in solution becomes higher by increased rigidity of the main chain.[37] **P(O*)** is by far the most rigid polymer and has the highest quantum yield. For all

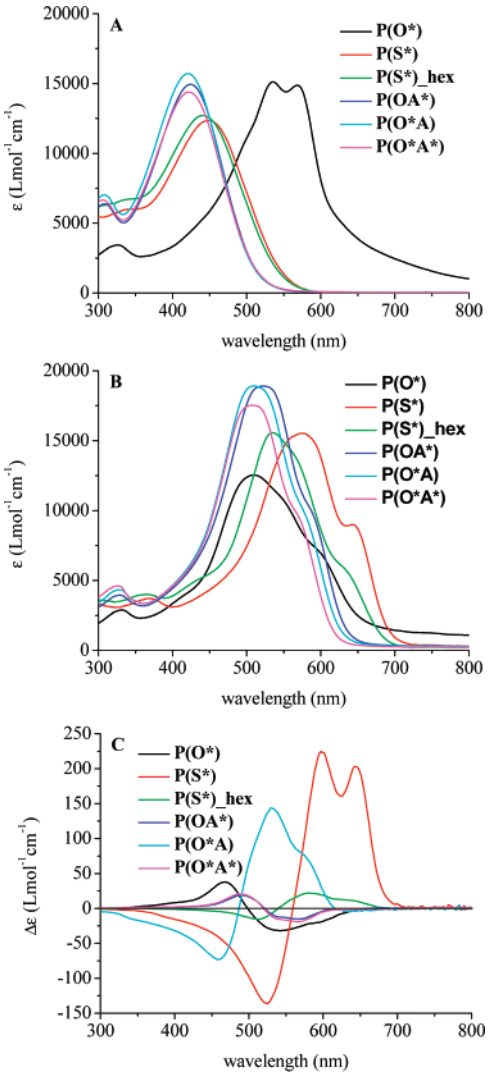


Figure 2. UV−vis spectra of **P(O*)**, **P(S*)**, **P(S*)_hex**, **P(OA*)**, **P(O*A)**, and **P(O*A*)** in (A) chloroform and (B) a chloroform/methanol mixture ($^1/_9$), and (C) CD spectra in a chloroform/methanol mixture ($^1/_9$) (c = 30 mg/L).

Table 4. Emission Data of the Polymers in Chloroform

polymer	λ_{ex}/nm	λ_{em}/nm	fwhm$_{em}$/cm^{-1}	Stokes shift/cm^{-1}	Φ_f[a]
P(O*)	520	589	1685	1679	0.43
P(S)	430	574	2596	4949	0.26
P(S*)	430	576	2596	4911	0.27
P(S*)_hex	420	567	2893	4987	0.27
P(OA)	400	546	2986	5270	0.23
P(OA*)	400	546	3035	5214	0.25
P(O*A)	400	540	3107	5178	0.25
P(O*A*)	400	542	3080	5247	0.30

[a] Measured toward cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol).

polymers, full fluorescence quenching was achieved upon addition of nonsolvent (MeOH).

It is clear that all spectroscopic data discriminate the dialkoxy-substituted PTT (**P(O*)**) from all other polymers: while **P(O*)** adopts a rather rigid, highly conjugated conformation in good solvents, the dialkylthio-substituted PTTs and the alternating copolymers are present as flexible, poorly conjugated random coils. Although all polymers aggregate in poor solvents, there is an important difference in their aggregation process: **P(O*)** starts aggregating from rigid rods, while all other polymers can self-assemble from flexible, random coils. This difference might explain the absence of macroscopic order in **P(O*)** and its presence in all other polymers.

Chiroptical Properties in Film. The UV−vis and CD spectra of films, spin coated from the chloroform solution, before and after annealing are shown in Figure 3. The UV−vis spectra resemble those of the polymers in poor solvents. A large red-shift, as compared to solutions in good solvents, was observed for the alkylthio-substituted polymers ($\Delta\lambda \sim 150$ nm) and the alternating copolymers ($\Delta\lambda \sim 90-120$ nm), accompanied by the appearance of a vibronic fine-structure, which becomes more pronounced after annealing.

The semi-crystalline polymers (**P(S$^{(*)}$)** and **P(O$^{(*)}$A$^{(*)}$)**) were annealed 5 °C below their melting temperature during 1 min. The amorphous polymer (**P(O*)**) was annealed at temperatures higher than the glass transition temperature during 1 min. These conditions were chosen since they appeared to result in the highest Cotton effects. The band gaps were calculated from the onset of the absorption band and range between 1.74 and 2.00 eV.

Analogous to the situation in poor solvent, **P(O*)** exhibits a rather weak, bisignate Cotton effect in film, indicative for chiral exciton coupling. A maximum g_{abs}-value of 6.4 × 10^{-3} was observed for this polymer. By annealing (1 min @ 160 °C, followed by 1 min @ 200 °C), however, this bisignate Cotton effect weakens (g_{abs} = 1.9 × 10^{-3}). Weak bisignate Cotton effects were also observed for **P(S*)_hex** and **P(OA*)** in film. After annealing, the bisignate Cotton effect is even inverted for both polymers. This phenomenon has also been observed in chiral polythiophenes[38] and can be attributed to the altered orientation of the stacked polymer backbones.

The CD spectra in film of all other polymers differ dramatically from their CD spectra in poor solvents. **P(S*)**, **P(O*A)** and **P(O*A*)** display asymmetric Cotton effects which are of much higher intensity than in a poor solvent. After annealing, g_{abs}-values up to 7.0 × 10^{-2} are obtained. In fact, their shape resembles those of chiral polyfluorenes (PFs).[20] Probably, the CD spectra of **P(S*)**, **P(O*A),** and **P(O*A*)** are a superposition of several Cotton effects. Quite likely, as is the case in poor solvents, bisignate Cotton effects, arising from chiral exciton coupling between chirally stacked polymer chains, are still present. Another contribution might originate from a chiral, helical conformation of the polymer backbone itself. However, it is very unlikely that this is the sole explanation for the difference in the CD spectra in poor solvents (only chiral exciton coupling) and films (chiral exciton coupling plus other contributions). In fact, if the polymer backbone of these polymers would adopt a helical conformation in film, it would probably also do so in poor solvents and, as a consequence, the CD spectra in film would resemble those in poor solvents.

The fundamental difference between the situation in poor solvents and film is the fact that in poor solvents, the polymer is present in aggregates which are isotropically distributed in the solvent, while in a film (macroscopic), order is present and the morphology can become important. The aggregates, from which the films are constituted and which are likewise present in poor solvent, consist of (chirally) stacked polymer chains. This gives rise to the chiral exciton coupling and the resulting bisignate Cotton effects. However, due to a different history of the aggregates (difference in the way they are fabricated, annealing,...) the (chiral) orientation of the polymer strands toward each other in the aggregates might differ as well. This can result in a different sign and magnitude of the Cotton effects (for instance, the inversion of the Cotton effect after annealing), but it cannot explain the difference in shape.

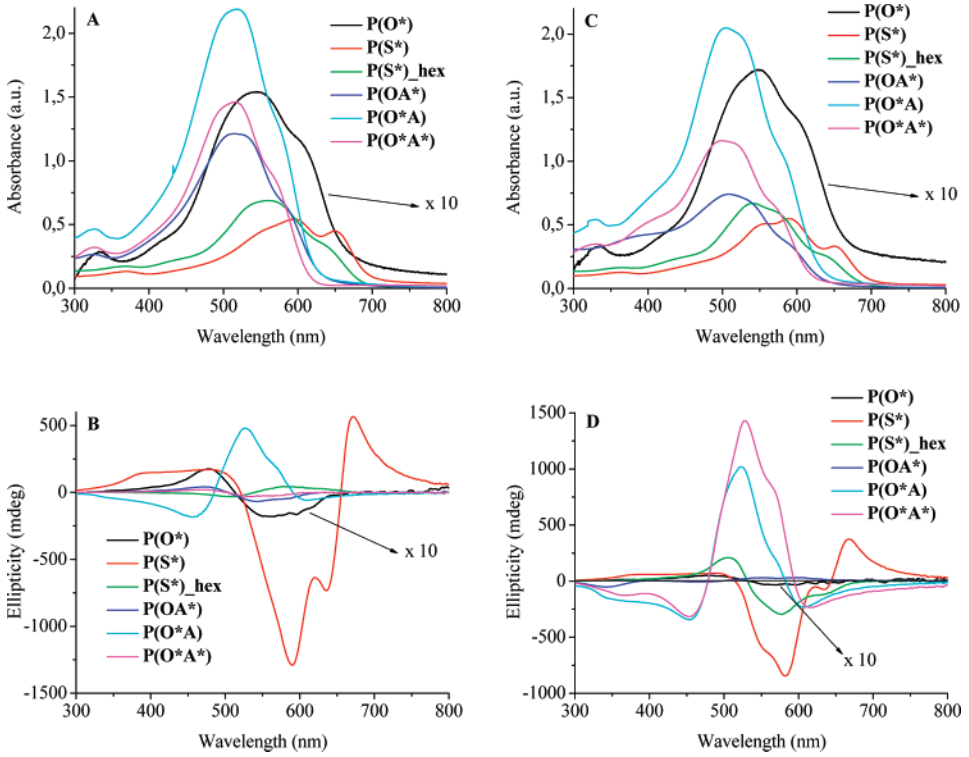


Figure 3. (A) UV−vis and (B) CD spectra of films before annealing; (C) UV−vis and (D) CD spectra of films after annealing

It is important to take into account that **P(S$^{(*)}$)** and **P(O$^{(*)}$A$^{(*)}$)** are semi-crystalline materials and that (macroscopic) order must be present in their films. As already mentioned, the CD spectra of **P(S*)**, **P(O*A)**, and **P(O*A*)** resemble those of PFs. Chiral, *liquid-crystalline* PFs and oligofluorenes exhibit asymmetric CD spectra with extremely large g_{abs}-values (>0.15). In PF, the shape of the CD band was explained as a combination of *inter*chain exciton coupling (*inter*chromophore interactions) and a chiral (helical) *intra*chromophore conformation.[20c] For the oligofluorenes, however, it has been shown that cholesteric stacking is the main contribution to the CD bands.[39] Very high g_{abs}-values in combination with asymmetric CD spectra have also been observed in annealed films of chirally substituted, *liquid-crystalline* poly(phenylene ethynylene)s (PPEs). Here, the Cotton effects were explained by the presence of helically twisted bundles of planar chains.[19] The above-mentioned observations suggest that liquid crystallinity might explain the exceptional Cotton effects. Therefore, it was investigated whether our polymers show liquid-crystalline behavior. However, extensive polarized UV−vis spectroscopy experiments indicated that all our polymers are *not* liquid-crystalline. Nevertheless, it must be remarked that the same phenomena that invoke the exceptional CD spectra in liquid-crystalline oligo- (and poly)fluorenes, can likewise invoke the unusual, observed CD of films of **P(S*)**, **P(O*A)**, and **P(O*A*)**. The exceptional CD spectra of films of **P(S*)**, **P(O*A)**, and **P(O*A*)** can therefore be explained by the presence of additional contributions originating from the macroscopic order. For instance, contributions from light scattering, resulting from the macroscopic order, to the CD signals cannot be ruled out. Probably, the Cotton effect around 700 nm in films of **P(S*)** originates from a difference in scattering intensity of left and right polarized light.

Another intriguing feature of these polymers is the thickness dependence of their Cotton effects. The thickness dependence of **P(S*)** was investigated by evaluating the chiroptical properties of films of different thickness (**P(S*)$_{1-5}$**), which were prepared by varying the concentration of the spin coat solution (Figure 4). The films were prepared from chloroform solutions, and the spectra were recorded before and after annealing. The g_{abs}-values of **P(S*)$_{1-5}$** at the dominant CD peak (589 nm) are summarized in Table 5. In case of "real" circular dichroism, as for instance in HT-P3ATs, the g_{abs}-values must be *in*dependent on the film thickness. In that case, g_{abs}-values in the order of $10^{-3}-10^{-2}$ are typically observed.[40] In **P(S*)$_{1-5}$**, however, a clear thickness dependence in combination with high g_{abs}-values ($>10^{-2}$) is observed.

The exceptional high g_{abs}-values in chiral, annealed PF films was explained by Craig et al. by "pseudo" circular dichroism.[41] Apart from "real" circular dichroism, the statistical difference in absorption of left and right circular light, "pseudo" circular dichroism increases the overall difference in absorption. In the case of "pseudo" circular dichroism, a clear thickness dependence of the g_{abs}-values is expected. For "pseudo" circular dichroism to be present, only mesoscale ordering is necessary, so liquid crystallinity is not strictly required. For instance, significant contributions from "pseudo" circular dichroism were observed in chiral poly(phenylene-*alt*-bithiophene)s, although they are not liquid-crystalline as well.[33]

Interestingly, **P(S*)** and **P(S*)_hex** show different CD behavior. Lower molecular-weight **P(S*)_hex** still exhibits a rather bisignate shape, while higher molecular-weight **P(S*)$_{1-5}$** show asymmetric CD spectra. This implies that only chiral *inter*chain interactions are responsible for the CD spectrum of the lower molecular-weight material.

Oxidation Behavior in Solution and Film. The absorption maxima of oxidized polymers are summarized in Table 3. Films of **P(S)**, **P(S*)**, and **P(S*)_hex** were readily dedoped after oxidation if iodine is used as an oxidant. However, all polymers could be oxidized in solution as well as in thin film using $NOBF_4$ as the oxidating agent. Upon doping with $NOBF_4$, the absorption in the visible region disappears and two new absorption peaks arise: one around 800−900 nm and one >2000 nm.

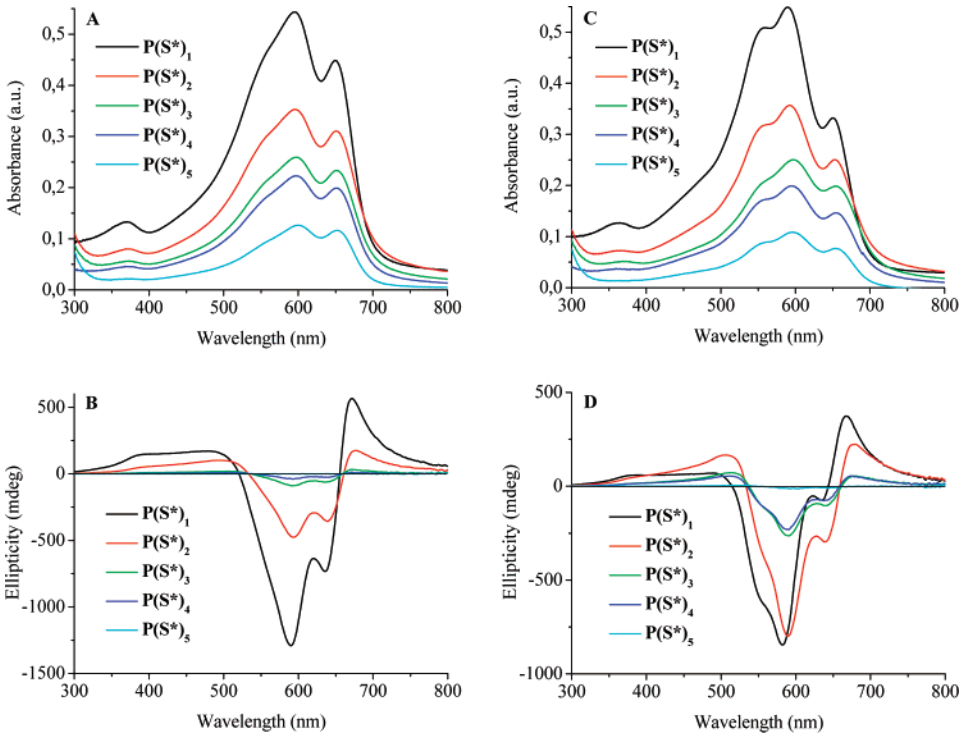


Figure 4. Thickness dependence of **P(S*)**; (A) UV−vis and (B) CD spectra of films before annealing; (C) UV−vis and (D) CD spectra of films after annealing.

Table 5. g_{abs}-Values of the Polymers in Film Before and After Annealing

polymer	$\|g_{abs}\|$ before annealing/10^{-3}	$\|g_{abs}\|$ after annealing[a]/10^{-3}	$\lambda_{\|g_{abs}\|}$[b]/nm
P(O*)	6.4	1.9	463
P(S*)$_1$	73	48	589
P(S*)$_2$	41	70	589
P(S*)$_3$	11	33	589
P(S*)$_4$	5.4	36	589
P(S*)$_5$	0.33	3.6	589
P(S*)_hex	2.3	15	579
P(OA*)	2.2	1.8	573
P(O*A)	6.8	16	529
P(O*A*)	0.74	41	535

[a] All polymer films were annealed for 1 min: **P(O*)** @ 200 °C; **P(S*)$_{1-5}$** @ 150 °C; **P(S*)_hex** @ 120 °C; **P(OA*)** @ 180 °C; **P(O*A)** @ 150 °C; **P(O*A*)** @ 145 °C. [b] Wavelength where the g_{abs}-value was determined (before and after annealing).

Koizumi et al. have indicated that dedoping of poly(alkylthiophene)s proceeds via a deprotonation of an α-H.[42] This might suggest that the stability of substituted polythiophenes and their derivatives in general depends on the absence of α-H. However, the iodine-doped thioalkyl-substituted PTTs show a very unstable oxidized state while they lack any α-Hs. This implies that the absence of α-Hs alone does not suffice for a polymer to have a stable oxidized state and that the oxidation potential of the polymer remains an important factor.

Conclusion

In conclusion, we have prepared three, differently substituted PTTs by Stille-coupling reactions: poly(3,6-dialkoxythieno[3,2-*b*]thiophene)s, poly(3,6-dialkylthiothieno[3,2-*b*]thiophene)s, and a series of alternating copolymers of 3,6-dialkoxythieno[3,2-*b*]-thiophenes with 3,6-dialkylthieno[3,2-*b*]thiophenes. The (chir)-optical properties of the polymers were investigated and appeared to depend significantly on the substituent used. In dialkoxy-substituted PTTs, strong S−O interactions between neighboring TT units are present, which, together with the small steric hindrance, results in highly conjugated, rigid, rod-like structures in solution. In the alternating copolymers, however, the S−O interactions are weakened and the steric hindrance between neighboring TT units is increased. As a consequence, these materials can adopt a flexible, poorly conjugated, random coil-like structure in solution. Substitution with alkylthio groups has a similar effect. Upon transition to films or in nonsolvents, all polymers aggregate, but, while the aggregation process of **P(O*)** consists of the stacking of rigid rods, all other polymers can self-assemble from flexible, random coils. This difference might explain the absence of macroscopic order in **P(O*)** and its presence in all other polymers. The Cotton effects in nonsolvents are due to chiral exciton coupling, but the CD spectrum of some semi-crystalline polymers, however, proved to have several contributions, among which "real" circular dichroism, "pseudo" circular dichroism, and contributions due to macroscopic order. Given their good solubility and film forming ability, high order, and relative low band gap, these polymers hold promise for the construction of FETs and solar cells.

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Supporting Information Available: UV−vis and CD spectra demonstrating the influence of the chloroform/methanol ratio of **P(S*)**, CV spectra of all polymers, ^{1}H NMR spectra of all polymers, ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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