Macromolecules **2008,** *41,* 591−598

Chiroptical Properties of Cyclopentadithiophene-Based Conjugated Polymers

Lieven De Cremer, Steven Vandeleene, Maarten Maesen, Thierry Verbiest, and Guy Koeckelberghs*

Laboratory of Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee (Leuven), Belgium

Received October 19, 2007; Revised Manuscript Received November 28, 2007

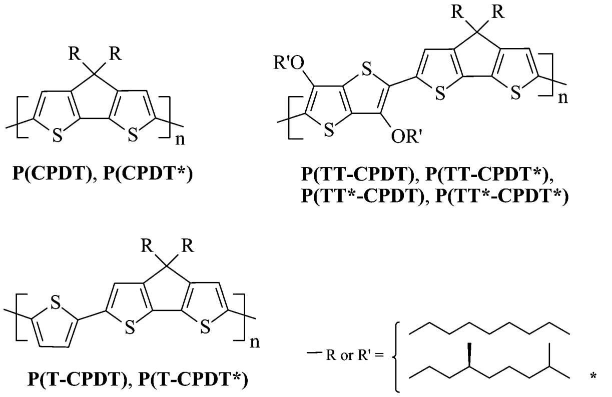
ABSTRACT: A series of chiral, substituted conjugated polymers containing the cyclopenta[2,1-*b*:3,4-*b*′]dithiophene unit were synthesized: poly(cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s, poly(thieno[3,2-*b*]thiophene-*alt*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene)s and poly(thiophene-*alt*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s. The polymers were prepared by a Stille-coupling reaction and their (chir)optical properties were investigated in solution as well as in film. UV−vis and fluorescence spectroscopy indicated that the polymers are present as rigid, highly conjugated strands in solution. Although the homopolymers (poly(cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s) do not self-assemble in solution as well as in film, the alternating copolymers (chirally) stack upon transition to nonsolvents and solid state. The (chir)optical properties in film appeared to depend on the annealing conditions: initially, the chiroptical response increases, but at higher temperatures, the Cotton effects irreversibly disappear. Moreover, the CD spectra of films of poly(thieno[3,2-*b*]thiophene-*alt*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s with chiral substituents on the thieno[3,2-*b*]thiophene moiety appeared to be a superposition of two effects, which had a different annealing dependency. In poly(thiophene-*alt*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s, only chiral exciton coupling was found to be present.

Introduction

Substituted poly(cyclopentadithiophene)s (PCPDTs) and their derivatives constitute a promising class of solution-processable, low band gap conjugated polymers. These materials are based on the rigid nature of cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) and can be regarded as fused-ring analogues of poly(3-alkylthiophene)s (P3ATs) and structural analogues of polyfluorenes (PFs). Regioregular P3ATs (HT-P3ATs) show a unique macromolecular self-assembly into semicrystalline, ordered domains upon transition from solution (random coils) to films (aggregates). As a consequence, these materials have demonstrated great potential as active layers in various applications in microelectronics and electro-optics.[1] Also the macromolecular and supramolecular behavior of substituted PFs has been the subject of many studies. PFs are known to show a broad variety of structures in the condensed state, including nematic liquid crystalline mesophases and crystalline phases.[2] Also alternating copolymers of fluorenes and other aromatic moieties, such as thieno[3,2-*b*]thiophene, have been prepared.[3] These materials possess highly ordered, liquid crystalline morphologies in solid state as well.

Dialkyl-substituted PCPDTs were shown to be highly conjugated ($\lambda_{max} \sim 560-590$ nm) with a relatively low band gap ($E_g \sim 1.8$ eV).[4−5] This is in contrast with PFs, which are characterized by rather poor conjugation lengths ($\lambda_{max} \sim 380$ nm) and relatively high band gaps ($E_g \sim 3.3$ eV).[2] For dialkyl-substituted PCPDTs, it has been shown that the absorption spectra in good solvents are nearly identical to the absorption spectra recorded in poor solvents and films (no bathochromic shift is observed). Because of an out-of-plane arrangement of the substituents on the polymer backbone, these polymers cannot self-assemble into ordered structures.[5] As a consequence, poor charge carrier mobilities ($\mu \sim 8 \times 10^{-5}$ cm^2/(V s)) were measured for these materials.[6]

Chart 1. Structure of the Polymers



It is an intriguing fact that PFs readily self-organize into ordered states, while their structural analogues, PCPDTs, do not aggregate in nonsolvents and solid state. Nevertheless, in order to apply CPDT-based polymers as charge transport materials in electronic devices, efficient π-stacking between the polymer strands is indispensable. Since the rate-limiting step for charge transport is interchain hopping, this process is maximized by close π-stacking.[7]

Several approaches to overcome the problem of excessive steric hindrance in dialkylated PCPDTs have been developed. First, monosubstitution instead of disubstitution was investigated. In monoalkyl-substituted PCPDTs, π-stacking is present, and as a consequence, relatively high conductivities (up to 300 S/cm) were reported.[4] These polymers, however, proved to have a poor solubility. Second, alkenyl-bridged PCPDTs, which have an in-plane arrangement of the substituents onto the polymer backbone, were developed.[8] They show significant bathochromic shifts (up to 80 nm) upon transition from solution to solid state.

---

* Corresponding author. E-mail: guy.koeckelberghs@chem.kuleuven.be.

10.1021/ma7023304 CCC: $40.75

Scheme 1. Synthesis of the Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene Monomers

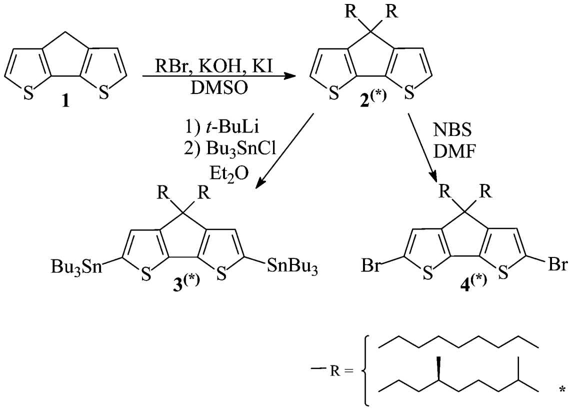


Table 1. Yield, Molecular Weight, Polydispersity, and Electrochemical Data of the Polymers

polymer	yield^a/%	$\bar{M}_n{}^b/10^4$ g·mol^{-1}	PDI^b	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V
P(CPDT)	81^c	12.1	14	0.47	0.28	0.38
P(CPDT*)	75	7.36	18	0.55	0.29	0.42
P(TT-CPDT)	83	90.8	2.6	0.46	0.32	0.39
P(TT-CPDT*)	84	59.8	3.9	0.49	0.34	0.42
P(TT*-CPDT)	68	43.3	3.1	0.43	0.36	0.39
P(TT*-CPDT*)	74	12.3	7.0	0.57	0.34	0.45
P(T-CPDT)	55^c	120	2.0	0.70	0.35	0.53
P(T-CPDT*)	56	210	2.2	0.69	0.44	0.57

[a] Of the *n*-hexane-soluble fraction. [b] Determined by GPC in THF toward polystyrene standards. [c] Of the chloroform-soluble fraction.

It was shown that extensive π-stacking is present in these materials. Finally, very recently, an alternating copolymer of dialkyl-substituted CPDT and benzothiadiazole was constructed.[9] Although the copolymer was amorphous, the material exhibit the ability to self-assemble into a lamellar superstructure. It has provided functionally desirable OFET performance characteristics with mobilities up to 0.17 cm^2/(V s), when solution deposited.[9a]

In this work, we report the synthesis and chiroptical behavior of CPDT-based alternating copolymers which have the ability to aggregate in nonsolvents and solid state. Two different aromatic moieties—3,6-dialkoxy-substituted thieno[3,2-*b*]thiophene (TT) and thiophene (T)—were used as comonomer. For comparison, dialkyl-substituted PCPDTs were synthesized as well (Chart 1). The (chiral) aggregation of the polymers was investigated using circular dichroism (CD) spectroscopy. For that purpose, also chiral polymers were prepared. By the best of our knowledge, this is the first example of optically active, CPDT-based polymers. Throughout the manuscript, the asterisk (*) denotes the chiral substituent.

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) as eluent toward polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. 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 counterelectrode and working electrode, respectively. The measurements were done in acetonitrile with Bu_4NBF_4 (0.1 M) as the supporting electrolyte under argon atmosphere. Therefore, the solution was purged with argon for 30 s. 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.[10] The optical rotations were measured with a polAAr 20 apparatus; the solvent used and concentration (in g/100 mL) are given in parenthesis. Films for UV−vis and CD experiments were prepared by spin-coating from chloroform solution (1500 rpm, 10 s).

Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**1**),[5c] 4,4-dioctylcyclopenta-[2,1-*b*:3,4-*b*′]dithiophene (**2**),[5c] 2,6-dibromo-4,4-dioctylcyclopenta-[2,1-*b*:3,4-*b*′]dithiophene (**4**),[5c] 2,5-di(trimethyltin)-3,6-dioctyloxythieno[3,2-*b*]thiophene (**5**),[11] (3*S*,3′*S*)-(+)-2,5-di(trimethyltin)-3,6-di(3,7-dimethyloctyloxy)thieno[3,2-*b*]thiophene (**5***),[11] 2,5-di(trimethyltin)thiophene (**6**),[12] and (*S*)-(+)-1-bromo-3,7-dimethyloctane[13] were synthesized according to literature procedures.

Synthesis of (3*S*,3′*S*)-(+)-4,4-di(3,7-dimethyloctyl)cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene (2*). At 0 °C and under argon atmosphere, grinded KOH (1.00 g, 17.8 mmol) was added in portions to a solution of **1** (1.00 g, 5.60 mmol), (*S*)-(+)-1-bromo-3,7-dimethyloctane (3.10 g, 14.0 mmol), and KI (25.0 mg, 150 μmol) in DMSO (25 mL). After overnight stirring at room temperature, the solution was cooled in an ice bath and water (25 mL) was added. The crude compound was extracted with hexanes and extensively washed with water and a saturated NH_4Cl solution. After being dried over anhydrous $MgSO_4$, the solvent was removed in vacuo. The crude compound was purified by column chromatography (silica gel; eluent: hexanes) and isolated as a clear oil.

Yield: 4.96 g (77%).

$[\alpha]_D^{20} = +3.60$ deg·dm^{-1}·mol^{-1}·L ($c = 2.0$ in dichloromethane).

^{1}H NMR ($CDCl_3$): $\delta = 7.12$ (d, 2H, $J = 4.6$ Hz), 6.91 (d, 2H, $J = 4.6$ Hz), 1.82 (m, 4H), 1.46 (m, 2H), 1.0−1.3 (m, 12H), 0.93 (m, 4H), 0.83 (d, 12H), 0.78 (m, 2H), 0.74 (d, 6H).

^{13}C NMR ($CDCl_3$): $\delta = 158.2$, 136.7, 124.6, 121.8, 53.2, 39.4, 37.0, 35.1, 33.2, 31.4, 28.1, 24.8, 22.9, 22.8, 19.8.

MS: $m/z = 459.3$ (M^+) (calcd 458.9).

Synthesis of 2,6-di(tributyltin)-4,4-dioctylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene (3). At 0 °C and under argon atmosphere, *t*-BuLi (1.40 mL, 2.10 mmol, 1.5 M in pentane) was cannulated into a solution of **2** (403 mg, 1.00 mmol) in dry diethyl ether (50 mL). The reaction was stirred for 15 min at room temperature and Bu_3SnCl (0.60 mL, 2.21 mmol) was added via syringe. After overnight stirring 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 isolated as a yellow, viscous oil, which was used without further purification.

Yield: 971 mg (99%).

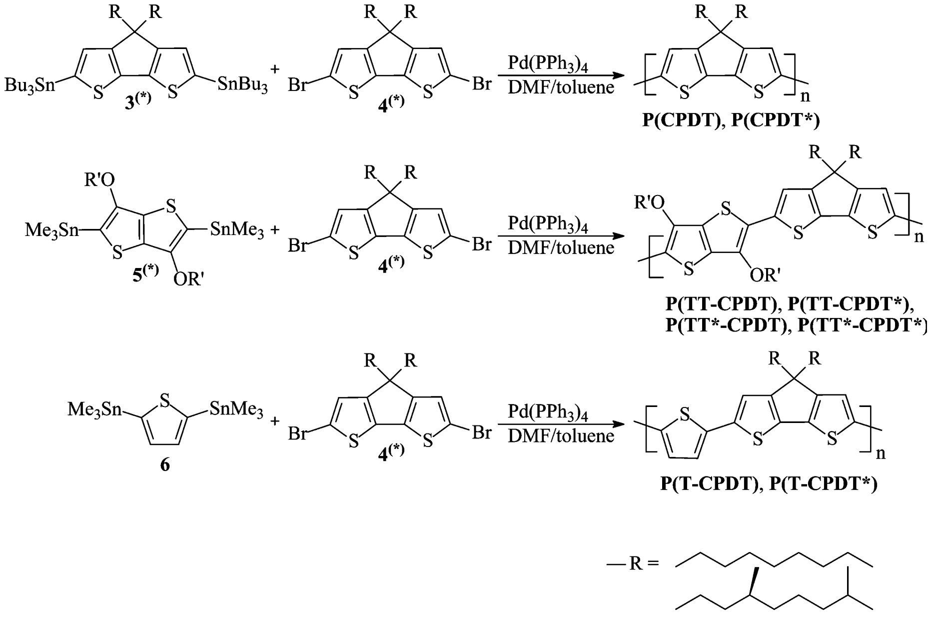
^{1}H NMR ($CDCl_3$): $\delta = 6.90$ (s, 2H), 1.80 (m, 4H), 1.58 (m, 12H), 1.34 (m, 12H), 1.0−1.3 (m, 32H), 0.99 (m, 4H), 0.8−1.0 (m, 24H).

^{13}C NMR ($CDCl_3$): $\delta = 160.4$, 142.4, 135.9, 129.8, 52.2, 37.9, 32.0, 30.2, 29.5, 29.4, 29.2, 27.4, 24.8, 22.8, 14.3, 13.8, 11.0.

MS: $m/z = 980.7$ (M^+) (calcd 980.9).

Synthesis of (3*S*,3′*S*)-(+)-2,6-di(tributyltin)-4,4-di(3,7-dimethyloctyl)cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (3*). Compound **3*** was obtained from **2*** (459 mg, 1.00 mmol), following a similar procedure as described for **3**. After removal of the salts, the crude compound was isolated as a yellow, viscous oil, which was used without further purification.

Scheme 2. Synthesis of the Polymers



Yield: 1.03 g (99%).

$[\alpha]_D^{20} = + 2.60$ deg·dm^{-1}·mol^{-1}·L (c = 2.0 in dichloromethane).

^{1}H NMR (CDCl$_3$): $\delta = 6.89$ (s, 2H), 1.81 (m, 4H), 1.58 (m, 12H), 1.47 (m, 2H), 1.34 (m, 12H), 1.0−1.3 (m, 24H), 0.8−1.0 (m, 36H), 0.74 (d, 6H).

^{13}C NMR (CDCl$_3$): $\delta = 160.4$, 142.5, 135.9, 129.8, 52.0, 39.4, 37.1, 35.2, 33.2, 31.7, 29.2, 28.1, 27.4, 24.9, 22.9, 22.8, 19.9, 13.9, 11.0.

MS: $m/z = 1036.4$ (M$^+$) (calcd 1037.0).

Synthesis of (3*S*,3′*S*)-(+)-2,6-dibromo-4,4-di(3,7-dimethyloctyl)cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (4*). A solution of **2*** (2.29 g, 5.00 mmol) in dry DMF (50 mL) was shielded from light and brought under argon atmosphere. At 0 °C, *N*-bromosuccinimide (1.87 g, 10.5 mmol) was added and the reaction mixture was allowed to reach room temperature and was further stirred overnight. After diluting the solution with diethyl ether, the organic layer was thoroughly washed with water, a saturated NaHCO$_3$ solution and dried over anhydrous MgSO$_4$. The solvent was removed in vacuo, and the crude compound was purified by column chromatography (silica gel; eluent = hexanes) and isolated as a yellow oil.

Yield: 2.47 g (80%).

$[\alpha]_D^{20} = + 4.53$ deg·dm^{-1}·mol^{-1}·L (c = 2.1 in dichloromethane).

^{1}H NMR (CDCl$_3$): $\delta = 6.92$ (s, 2H), 1.76 (m, 4H), 1.48 (m, 2H), 1.0−1.3 (m, 12H), 0.94 (m, 4H), 0.84 (d, 12H), 0.79 (m, 2H), 0.75 (d, 6H).

^{13}C NMR (CDCl$_3$): $\delta = 156.0$, 136.5, 124.6, 111.2, 55.0, 39.3, 36.9, 34.9, 33.1, 31.3, 28.1, 24.8, 22.8, 22.8, 19.7.

MS: $m/z = 616.1$ (M$^+$) (calcd 616.6).

Synthesis of the Polymers. A general procedure was as follows: A solution of distannylated monomer (300 μmol), dibrominated monomer (300 μmol), and 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 40 h. After the solution was cooled down to room temperature, the polymer was concentrated and poured into methanol. The polymer was filtered off and further purified by Soxhlet extractions using successively acetone, *n*-hexane, and chloroform. The chloroform-soluble fraction (or the *n*-hexane-soluble fraction in the case of complete solubility in *n*-hexane) was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

Results and Discussion

Monomer and Polymer Synthesis. The synthesis of the CPDT monomers is displayed in Scheme 1. Dialkylation of **1** was achieved using KOH as base in DMSO. The distannylated monomers **3** and **3*** were prepared by dilithiation of **2** and **2*** respectively, using *t*-BuLi, followed by quenching with Bu$_3$SnCl. The tin compounds are oils which could not be purified by column chromatography (since destannylation occurs).[14] Fortunately, they were sufficiently pure after reaction to be used without further purification. Bromination was accomplished using *N*-bromosuccinimide (NBS) in DMF.

The synthesis of the polymers is depicted in Scheme 2. All polymers were synthesized by a Stille cross-coupling reaction of distannylated and dibrominated monomers. In order to be able to investigate the chiroptical properties of the polymers, chiral polymers were prepared as well.

After polymerization, all polymers were washed with acetone and *n*-hexane using a Soxhlet apparatus to remove byproducts and low-molecular weight oligomers. Finally, the polymers were extracted with chloroform, precipitated into methanol and dried. Except for **P(CPDT)** and **P(T-CPDT)**, however, all polymers 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). DSC analysis, finally, indicated that, although not for all polymers clear thermal transitions were observed, none of the polymers show a crystallization peak below 250 °C. The glass transitions of the polymers vary between 150 and 240 °C. All polymers did not degrade below 250 °C.

Yield and GPC Analysis. The yields and molecular weights are summarized in Table 1. High yields (55−81% after Soxhlet extractions) were obtained. The molecular weights were determined by GPC in THF toward polystyrene standards. At first inspection, they seem very large. However, as will be shown, the polymers adopt a planar, rigid conformation in solution. Therefore, the hydrodynamic volumes of the polymers and the standards (polystyrene) differ significantly and, as a consequence, the value of the molecular weights determined must be put into perspective. It has, for instance, been shown that GPC typically overestimates the molecular weights of polymers which adopt a rigid-rod-like conformation if polystyrene standards are used.[15]

Electrochemical Behavior. The potential of the peak anodic current (E_{pa}) and peak cathodic current (E_{pc}) of films, drop casted

Table 2. Optical Data of the Polymers in Solution and Film

	λ_{max} in solution/nm					
	CHCl$_3$			λ_{max} in film/nm		
polymer	neutral	oxidized^a	CHCl$_3$/CH$_3$OH (1/9) neutral	neutral	oxidized^b	$E_g{}^c$/eV
P(CPDT)	588	1029, >2000	574	578	994, >2000	1.83
P(CPDT*)	588	1053, >2000	579	581	1025, >2000	1.84
P(TT-CPDT)	612	968, >2000	604, 646^d	596	954, >2000	1.79
P(TT-CPDT*)	611	967, >2000	601, 643^d	591	943, >2000	1.80
P(TT*-CPDT)	571	951, >2000	586	593	926, >2000	1.79
P(TT*-CPDT*)	572	929, >2000	583	588	926, >2000	1.79
P(T-CPDT)	588, 625^d	998, >2000	591, 624^d	573	961, >2000	1.83
P(T-CPDT*)	586, 621^d	1020, >2000	587, 626^d	572	1001, >2000	1.85

^{a} By addition of a concentrated NOBF$_4$ solution (in chloroform). ^{b} By exposure to NOBF$_4$ (in acetonitrile). ^{c} Optical band gap in film. ^{d} Two absorption maxima are observed (see Figure 1).

from chloroform solution onto the Pt working electrode, were measured using cyclic voltammetry. It is worthwhile to note that the E_{pa} value shifts to a lower potential after the first oxidation and back reduction cycle, indicating the formation of a more conjugated system. The E_{pc} value remained the same. After the second scan, the position and also the shape of the voltammograms remained roughly unchanged. Therefore, E_{pa} and E_{pc} were determined from the second scan. The oxidation processes of all polymers were quasi-reversible. The half-wave potential ($E_{1/2} = (E_{pa} + E_{pc})/2$) was independent of the scanning rate, and the oxidation and back-reduction could be repeated several times without significant change in the voltammogram.

The $E_{1/2}$ values of **P(CPDT)** and **P(CPDT*)** are respectively 0.38 and 0.42 V. For these polymers a second (broad) oxidation was observed at $E_{pa} \sim 0.85$ V. The onset of the oxidation wave was $\sim$ 0.35 V. From this value, the HOMO level can be calculated at $-$ 4.78 eV.[16] Interestingly, the alternating copolymers based on TT and CPDT have E_{pa}, E_{pc}, and $E_{1/2}$ values which are approximately the same as those of the CPDT-homopolymers ($E_{pa} \sim 0.5$ V, $E_{pc} \sim 0.3$ V, and $E_{1/2} \sim 0.4$ V). The same trend is observed for λ_{max} in a good solvent (see below). This observation indicates that the electronic properties of these alternating copolymers and the homopolymers do not significantly differ. The alternating copolymers from the less electron-rich thiophene moiety and the (a)chiral CPDT have higher E_{pa}, E_{pc}, and $E_{1/2}$ values. The onset of the oxidation wave was found at $\sim$0.50 V and the HOMO levels were calculated at $-$4.93 eV.[16]

Chiroptical Properties in Solution. The UV−vis data are summarized in Table 2. Representative UV−vis and CD spectra in good and poor solvents are shown in Figure 1. All polymers show already a strong conjugation in good solvent (chloroform) as evidenced by their rather high λ_{max} values (571−625 nm). In chloroform, no CD effects are observed. Upon addition of a nonsolvent (methanol), no or small bathochromic shifts are observed. This observation confirms that the polymers are already present as highly conjugated rods in good solvents and only slightly further planarize and possibly stack upon addition of a nonsolvent. Interestingly, a clear vibronic fine-structure appears for the copolymers (**P(TT$^{(*)}$-CPDT$^{(*)}$)** and **P(T-CPDT$^{(*)}$)**), while the homopolymers (**P(CPDT$^{(*)}$)**) show a less pronounced fine-structure in poor solvents. The difference between the homo- and copolymers becomes more clear in their CD spectra: In poor solvents, no CD effect is observed for **P(CPDT*)**. This observation confirms that 4,4-dialkyl-substituted PCPDTs do not aggregate in poor solvents. On the other hand—except for **P(TT-CPDT*)**—the chiral copolymers show bisignate Cotton effects in a nonsolvent mixture (chloroform/methanol (1/9)). These bisignate Cotton effects can be ascribed to chiral exciton coupling of chirally stacked, coplanar polymer strands.[17] The g_{abs} values ($g_{abs} = \Delta\epsilon/\epsilon$) of **P(TT*-CPDT)**, **P(TT*-CPDT*)**, and **P(T-CPDT*)** are 9 × 10^{-4}, 5 × 10^{-3}, and 5 × 10^{-4}, respectively, which are typical values for chiral exciton coupling of conjugated polymers in poor solvents.

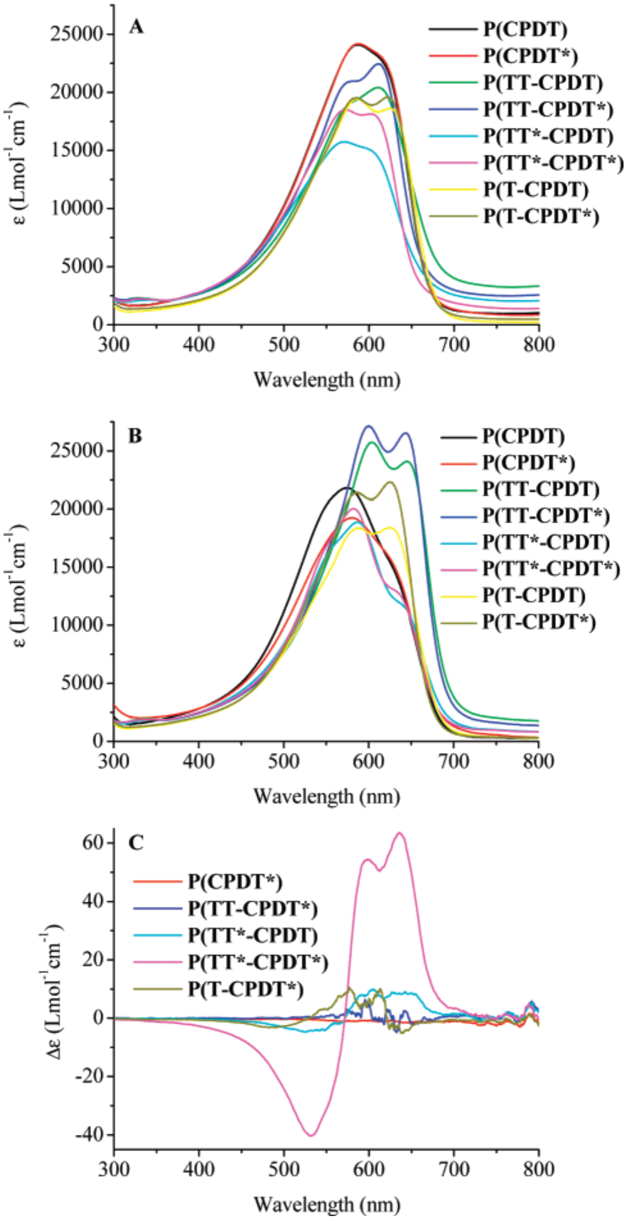


Figure 1. UV−vis spectra of the polymers in (A) chloroform and (B) a chloroform/methanol mixture (1/9) and C) CD spectra in a chloroform/methanol mixture (1/9) (c = 30 mg/L).

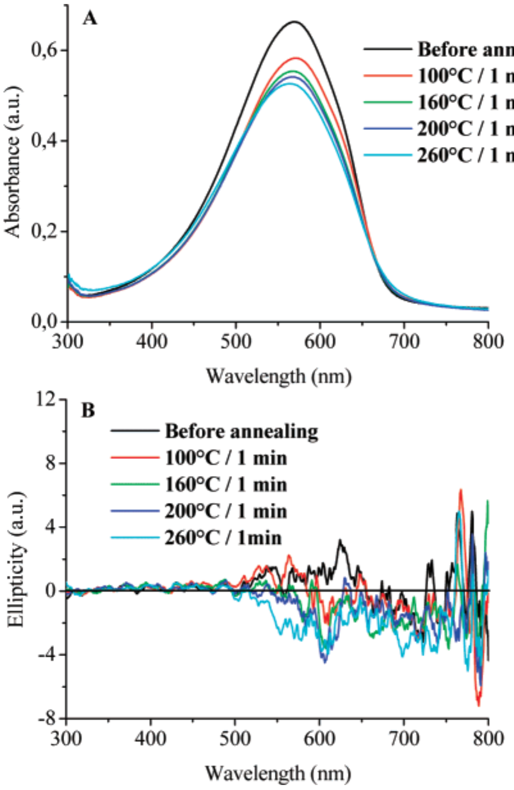


Figure 2. (A) UV−vis and (B) CD spectra of an annealed film of **P(CPDT*)**.

Because chiral exciton coupling is an *inter*molecular effect, it must be concentration dependent. Therefore, we first have studied the solvatochromism for **P(TT*-CPDT*)** using different chloroform/methanol mixtures (c = 30 mg/L) (Figure 1, Supporting Information). This indicates that starting from 60% methanol, the polymers start to aggregate, as evidenced by the appearance of bisignate Cotton effects. Next, the concentration dependence of the CD effect was investigated in a chloroform/methanol (4/6) mixture, in which spectra intermediate between those in pure chloroform and chloroform/methanol (1/9) were obtained, (Figure 2, Supporting Information). A clear concentration dependence of the bisignate Cotton effect was observed. This proves that the CD effect is *inter*molecular in nature and excludes the possibility of an *intra*molecular chiral conformation (for instance a chiral, helical backbone). The significant difference in CD intensity of the three chiral alternating copolymers of TT and CPDT can be explained by the fact that all three chiral alternating copolymers adopt (slightly) different supramolecular structures, with corresponding different CD spectra. This difference in CD intensity was also observed in, for instance, chiral poly(phenylene-*alt*-bithiophene)s[18] and chiral poly(3,6-dialkoxy-TT-*alt*-3,6-dialkyl-TT)s.[11]

From the observed chiroptical properties, it is clear that both homopolymers and alternating copolymers of 4,4-dialkyl-substituted CPDTs adopt a highly conjugated, planar conformation in good as well as poor solvent. The homopolymers do not aggregate in solution, which can be ascribed to an out-of-plane arrangement of the substituents onto the polymer backbone, preventing π-stacking. In the alternating copolymers, however, (chiral) aggregation is possible. This is in agreement with the proposed self-organization of alternating copolymers of CPDT and benzothiadiazole.[9]

Fluorescence. Solution emission data in chloroform for the polymers are summarized in Table 3. The polymers show emission between 624 and 653 nm. Fluorescence is particularly an interesting tool to probe the rigidity of the polymer backbone: the broadness of the fluorescence peak (fwhm$_{em}$) and the Stokes shift decrease with increasing rigidity. The fwhm$_{em}$ of the polymers are on the order of 1000−1600 cm^{-1}, which are typical values for conjugated polymers with a rigid structure in good solvents.[19] The same trend is present for the Stokes shifts: rigid polymers show small Stokes shifts (typical 2000 cm^{-1}),[19] while polymers which adopt a flexible conformation (random coils) show large Stokes shifts (typical 5000−6000 cm^{-1}).[20] From the narrow emission peaks and the small Stokes shifts, it can be concluded that all polymers are present as rigid (planar) structures in chloroform. Low quantum yields (1−13%) were determined toward cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol). This standard was chosen as a reference since its λ_{em} matches closely with those of the polymers.

Table 3. Emission Data of the Polymers in Chloroform

polymer	λ_{ex}/nm	λ_{em}/nm	fwhm$_{em}$^{a}/cm^{-1}	Stokes shift^b/cm^{-1}	Φ_f^{c}/%
P(CPDT)	578	653	1293	1693	1.1
P(CPDT*)	578	651	1217	1646	1.0
P(TT-CPDT)	560	638	1051	666^d	6.5
P(TT-CPDT*)	560	641	983	766^d	7.1
P(TT*-CPDT)	561	628	1621	1589^e	13
P(TT*-CPDT*)	562	636	1107	1760^e	7.0
P(T-CPDT)	578	624	1235	981	3.8
P(T-CPDT*)	576	624	1288	1039	2.9

[a] Full width at half-maximum of the emission band. [b] Difference between the spectral positions of the band *maxima* of the absorption and emission. [c] Measured toward cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol). [d] These polymers have a λ_{max} ∼ 610 nm and an additional shoulder ∼570 nm in UV−vis. [e] These polymers have a λ_{max} ∼ 570 nm and an additional shoulder ∼600 nm in UV−vis.

Chiroptical Properties in Film. Representative UV−vis and CD spectra—before, during, and after annealing—of the chiral polymers are displayed in Figure 2−6. Upon transition from solution to film no or only slight bathochromic shifts are observed, which can be explained by the fact that the polymers are already planarized in solution. The optical band gaps were calculated from the onset of the absorption band and appeared to be approximately 1.80 eV.

As is the case in poor solvents, no CD effect was observed for **P(CPDT*)** in film (Figure 2). It is clear that this polymer does not (chirally) aggregate under any conditions. However, the copolymers do show circular dichroism (Figures 3−6) and the intensities of the CD bands increase by annealing. Interestingly, the Cotton effects of the TT-copolymers (**P(TT−CPDT*)**, **P(TT*-CPDT)**, and **P(TT*-CPDT*)**) decrease in intensity above a certain temperature (∼160 °C) and this disappearance was *irreversible*: If the sample was again heated to, for instance 100 °C, no Cotton effect appeared. After annealing at 160 °C, maximum g_{abs} values of 1 × 10^{-3} and 2 × 10^{-3} were achieved for **P(TT-CPDT*)** and **P(TT*-CPDT)**, respectively. A maximum g_{abs} value of 3 × 10^{-3} was obtained for **P(TT*-CPDT*)** after annealing at 100 °C. Except for **P(TT-CPDT*)**, the disappearance of the Cotton effects is accompanied by a decrease of the vibronic fine-structure. The same phenomenon was observed if the samples were stored: after storing the films for a couple of days at room temperature, the Cotton effects disappear, although no (visible) degradation had taken place. This suggest that for these materials a CD silent, probably less ordered structure is the thermodynamically most stable structure. It is important to emphasize that the (chiral) supramolecular order, as indicated by the presence of bisignate Cotton effects, relates to *meso*scale order and does not, therefore, conflict with the absence of *macro*scale order as suggested by DSC.

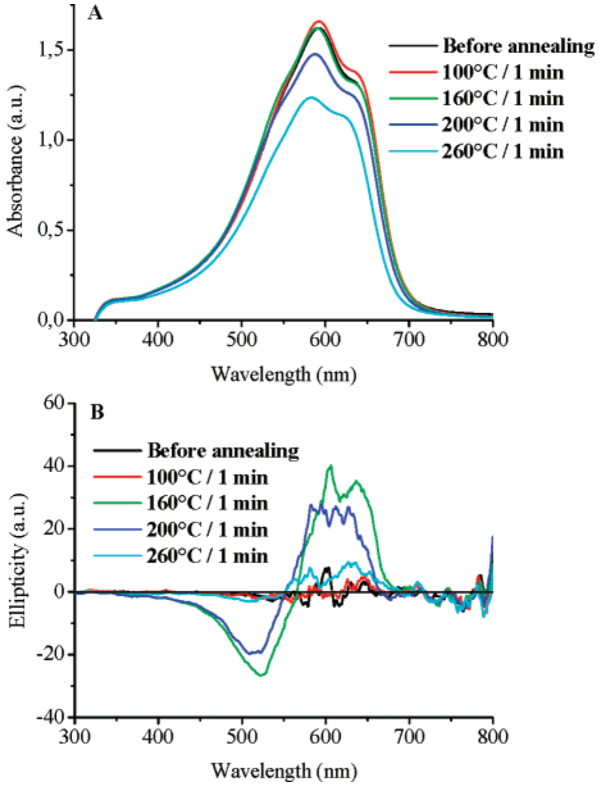


Figure 3. (A) UV−vis and (B) CD spectra of an annealed film of **P(TT-CPDT*)**.

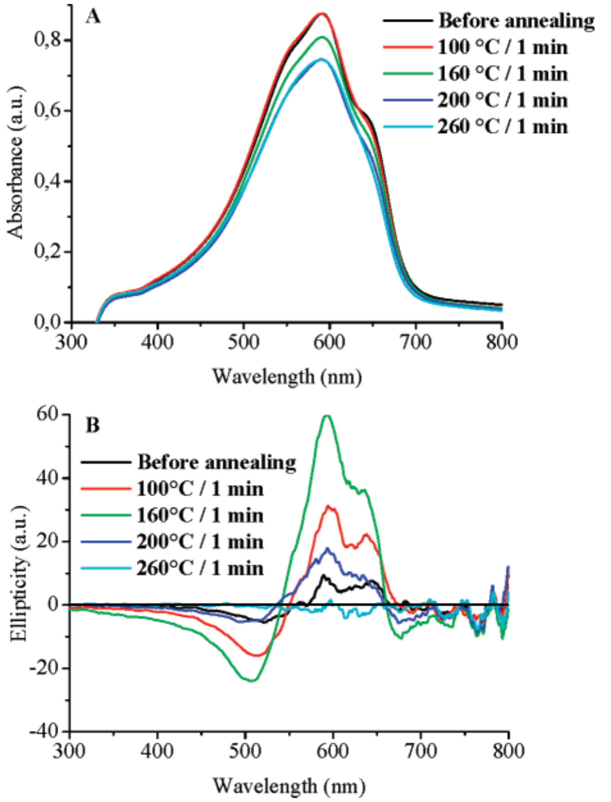


Figure 4. (A) UV−vis and (B) CD spectra of an annealed film of **P(TT*-CPDT)**.

Another intriguing feature is the *shape* of the CD spectra. The Cotton effects of films of **P(TT-CPDT*)** are clearly bisignate at all temperatures. This corresponds to chiral exciton coupling of chirally stacked polymers strands, analogous to the situation in nonsolvents. However, the copolymers with the chiral TT unit (**P(TT*-CPDT)** and **P(TT*-CPDT*)**) do *not* show a clear bisignate Cotton effect. The CD spectra seem to be a superposition of two spectra: a bisignate Cotton effect, arising from exciton coupling and a second CD effect. Since

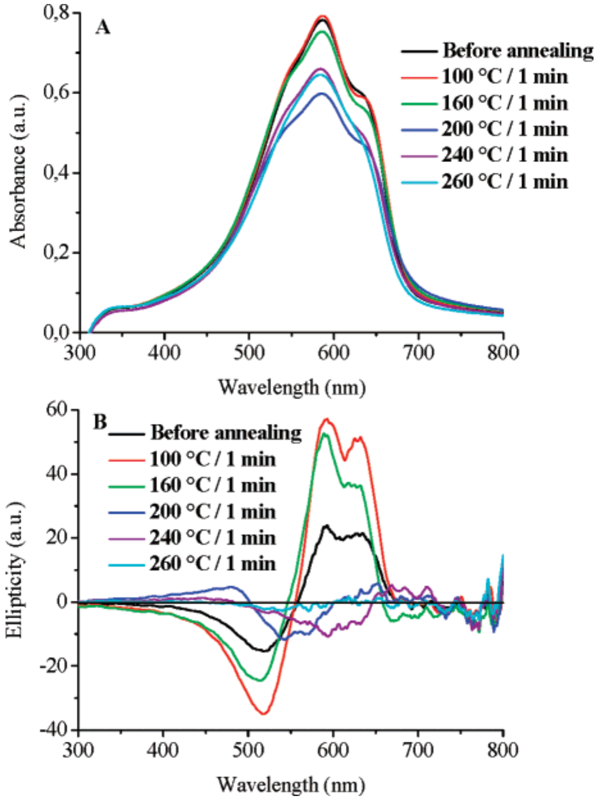


Figure 5. (A) UV−vis and (B) CD spectra of an annealed film of **P(TT*-CPDT*)**.

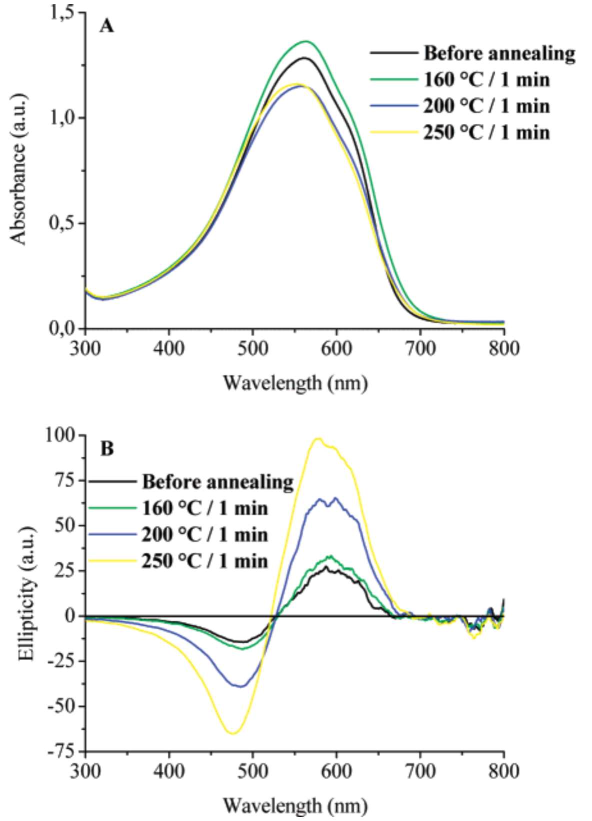


Figure 6. (A) UV−vis and (B) CD spectra of an annealed film of **P(T-CPDT*)**.

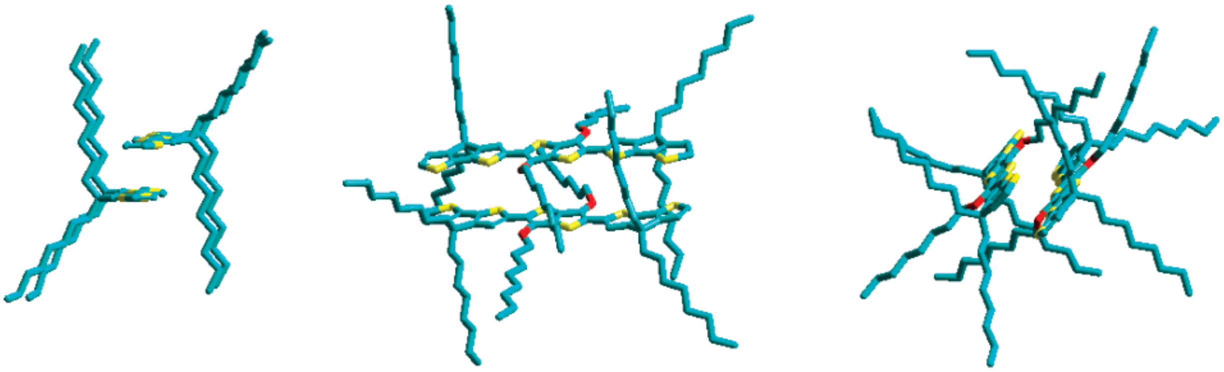


Figure 7. Presentation (calculated with hyperchem) of the stacking of **P(T-CPDT$^{(*)}$)** (left) and **P(TT$^{(*)}$-CPDT$^{(*)}$)** (middle and right).

both effects are likely to have different origins, their temperature dependence can be expected to be different as well. For instance, if **P(TT*-CPDT)** is annealed at 100 °C, the chiral exciton coupling seems to be the dominant factor, giving rise to a relatively clean bisignate Cotton effect. However, by heating the sample to 200 °C, the second effect becomes more important and the bisignate shape disappears. The same trend is observed for **P(TT*-CPDT*)**: by annealing at 100 °C, a clear bisignate Cotton effect is present, while at 200 °C, the CD spectrum becomes less intense and the bisignate shape disappears. At 240 °C, even a monosignate effect is observed. Clear bisignate Cotton effects were also observed for **P(T-CPDT*)**. Here no evidence for the existence of a monosignate effect was found. Upon annealing the bisignate Cotton effect increases. After annealing at 250 °C, the g_{abs} value is 3×10^{-3}.

While the origin of the bisignate Cotton effect is clear—chiral exciton coupling of chirally stacked polymer strands[17]—the origin of the second (monosignate) CD effect is unknown. Interestingly, it is only present in the copolymers with the chiral TT unit. One possible explanation might be that the alternating copolymers of TT and CPDT **P(TT$^{(*)}$-CPDT$^{(*)}$)** adopt a macromolecular chiral (helical) conformation, as is also the case in substituted poly(fluorene)s.[21] This conformation requires a twist from coplanarity between the alternating TT and CPDT units. This twist may be induced by the (chiral) substituent located on the TT unit. In that case, the presence (absence) of a chiral, helical backbone conformation depends on the presence (absence) of chiral substituents on the TT moiety. Consequently, in that case, the second (monosignate) Cotton effect is only present when a chiral TT* moiety is incorporated.

It is clear that, although both homopolymers and alternating copolymers of substituted CPDTs adopt a planar, highly conjugated conformation, only the copolymers can (chirally) aggregate. As already mentioned, steric hindrance, resulting from an out-of-plane arrangement of the substituents on the polymer backbone of **P(CPDT$^{(*)}$)**, prevents the stacking. If, however, an additional aromatic unit is incorporated in a regular way, as in alternating copolymers, this second unit creates some space which the substituents of a CPDT unit of another polymer strand can occupy. This allows two polymer strands to approach closely and stack. This is visualized in Figure 7. In the case of **P(T-CPDT$^{(*)}$)**, all substituents are located on one side of the polymer chain and two chains can easily approach and stack. In the case of the TT-copolymers (**P(TT$^{(*)}$-CPDT$^{(*)}$)**), the TT-moieties create additional space for the substituents on the CPDT-unit, again allowing two chains to approach and stack.

Oxidation Behavior in Solution and Film. All polymers can easily be oxidized in solution as well as in thin film using $NOBF_4$ as the oxidant. The ease of oxidation can be correlated with the electrochemical behavior of the polymer. The oxidized absorption maxima are summarized in Table 2. The blue color of the neutral solution/film is lost on doping and the doped solution/film becomes transparent. Remarkably, the oxidized polymers show a higher λ_{max} in solution than in film. This was also observed in *N*-alkyl-substituted poly(dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s and can be explained by the restricted mobility of the polymer backbone in film.[19b] Indeed, oxidation is accompanied by planarization (to stabilize the positive charge) and the required change in macromolecular structure (planarization) is more restricted in film than in solution. It is interesting to note that iodine-doped films of PCPDTs tend to spontaneously dedope relatively fast (in the order of minutes),[22] while $NOBF_4$-doped films of all polymers remained oxidized for extended periods of time (at least several hours to days).

Conclusion

In conclusion, we have prepared chiral, substituted homopolymers of 4,4-dialkylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene and alternating copolymers of 4,4-dialkylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene and a second aromatic group, i.e., (a)chiral 3,6-dialkoxythieno[3,2-*b*]thiophenes and thiophene. The polymers were synthesized by a Stille-coupling reaction. UV−vis and fluorescence spectroscopy indicated that all polymers are present as rigid, highly conjugated strands in solution. Although the homopolymers (poly(cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)s) do not aggregate in solution nor in film, the alternating copolymers (chirally) stack upon transition to nonsolvents and solid state, as indicated by UV−vis and CD spectroscopy. The (chir)optical properties in film depend on the annealing conditions: initially, the chiroptical response increases, but at higher temperatures, at which they attain the lowest-energy state, the Cotton effects irreversibly disappear. In films of the thienothiophene-containing copolymers with chiral substituents on the thienothiophene unit, the CD spectrum is a superposition of chiral exciton coupling and another contribution. The presence of (chiral) aggregation of the copolymers is explained by the possibility of two polymer chains to closely approach due to the creation of additional space by the incorporation of the second aromatic moiety.

Acknowledgment. We are grateful to the Katholieke Universiteit Leuven (GOA), the Fund for Scientific Research (FWO−Vlaanderen), Toyota Motor Company Europe, and the Air Force Office of Scientific Research, Air Force Material Command, USAF, under Grant No. FA8655-07-1-3004 for financial support. G.K. is a postdoctoral fellow of the Fund for Scientific Research (FWO−Vlaanderen).

Supporting Information Available: Figures showing the UV−vis and CD spectra demonstrating the influence of the chloroform/methanol ratio of **P(TT*-CPDT*)**, concentration dependence of the UV−vis and CD spectra of **P(TT*-CPDT*)** in a poor solvent mixture, absorption/emission spectra of all polymers in solution (chloroform), representative solution and solid state oxidation spectra, CV spectra of all polymers, ^{1}H NMR spectra of all polymers and ^{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.

References and Notes

(1) (a) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910−4911. (b) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244. (c) Jeffries-El, M.; McCullough, R. D. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press, Boca Raton, FL, **2007**; Vol. 1, pp 9/1−9/49.

(2) (a) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798−802. (b) Teetsov, J. A.; Vanden, Bout, D. A. *J. Am. Chem. Soc.* **2001**, *123*, 3605−3606. (c) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477−487. (d) List, E. J. W.; Scherf, U. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press, Boca Raton, FL, **2007**; Vol. 1, pp 5/1−5/35.

(3) (a) Lim, E.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 4288−4293. (b) Lim, E.; Jung, B.-J.; Lee, J.; Shim, H.-K.; Lee, J.-I.; Yang, Y. S.; Do, L.-M. *Macromolecules* **2005**, *38*, 4531−4535. (c) Lim, E.; Kim, Y. M.; Lee, J.-I.; Jung, B.-J.; Cho, N. S.; Lee, J.; Do, L.-M.; Shim, H.-K. *J. Polym. Sci. Pol. Chem.* **2006**, *44*, 4709−4721. (d) Tang, W.; Ke, L.; Tan, L.; Lin, T.; Kietzke, T.; Chen, Z.-K. *Macromolecules* **2007**, *40*, 6164−6171.

(4) (a) Zotti, G.; Schiavon, G.; Berlin, A.; Fontana, G.; Pagani, G. *Macromolecules*, **1994**, *27*, 1938−1942. (b) Benincori, T.; Consonni, V.; Gramatica, P.; Pilati, T.; Rizzo, S.; Sannicolò, F.; Todeschini, R.; Zotti, G. *Chem. Mater.* **2001**, *13*, 1665−1673.

(5) (a) Asawapirom, U.; Scherf, U. *Macromol. Rapid Commun.* **2001**, *22*, 746−749. (b) Coppo, P.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L. *J. Mater. Chem.* **2002**, *12*, 2597−2599. (c) Coppo, P.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L. *Macromolecules* **2003**, *36*, 2705−2711. (d) Coppo, P.; Turner, M. *J. Mater. Chem.* **2005**, *15*, 1123−1133. (e) Wu, C.-G.; Lu, M.-I.; Chang, S.-J.; Wei, C.-S. *Adv. Funct. Mater.* **2007**, *17*, 1063−1070.

(6) Coppo, P.; Turner, M. L.; Cupertino, D. C.; Yeates, S. G. *Mater. Res. Soc. Symp. Proc.* **2003**, *771*, 61−64.

(7) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053−1067.

(8) (a) Coppo, P.; Adams, H.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L. *Chem. Commun.* **2003**, 2548−2549. (b) Bünnagel, T. W.; Galbrecht, F.; Scherf, U. *Macromolecules* **2006**, *39*, 8870−8872.

(9) (a) Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C.; Mishra, A. K.; Müllen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3472−3473. (b) Soci, C.; Hwang, I.-W.; Moses, D.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. J.; Heeger, A. J. *Adv. Funct. Mater.* **2007**, *17*, 632−636. (c) Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Mühlbacher, D.; Scharber, M.; Brabec, C. *Macromolecules* **2007**, *40*, 1981−1986. (d) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497−500. (e) Palacios, R. E.; Fan, F.-R. F.; Grey, J. K.; Suk, J.; Bard, A. J.; Barbara, P. F. *Nat. Mater.* **2007**, *6*, 680−685.

(10) (a) *Standards in Fluorescence Spectroscopy*; Miller, J. N., Ed.; Chapman and Hall, New York, 1981; pp 68−78. (b) *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press, Boca Raton, FL, 1989; pp 233−236 and references therein.

(11) De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *Macromolecules*, in press.

(12) van Pham, C.; Macomber, R. S.; Mark, H. B., Jr.; Zimmer, H. *J. Org. Chem.* **1984**, *49*, 5250−5253.

(13) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157−160.

(14) Wu, C.-G.; Hsieh, C.-W.; Chen, D.-C.; Chang, S.-J.; Chen, K.-Y. *Synth. Met.* **2005**, *155*, 618−622.

(15) (a) Yamamoto, T.; Oguro, D.; Kubota, K. *Macromolecules* **1996**, *29*, 1833−1835. (b) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777−5785. (c) Sumi, N.; Nakanishi, H.; Ueno, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 979−988.

(16) Al-Ibrahim, M.; Roth, H.-K.; Zhokhavets, U.; Gobsch, G.; Sensfuss, S. *Sol. Energ. Mater. Sol. C.* **2005**, *85*, 13−20.

(17) Langeveld-Voss, B. M. W.; Beljonne, D.; Shuai, Z.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W.; Brédas, J.-L. *Adv. Mater.* **1998**, *10*, 1343−1348.

(18) Koeckelberghs, G.; Vangheluwe, M.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 8142−8150.

(19) (a) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771−1778. (b) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 4173−4181.

(20) (a) Belletête, M.; Mazerolle, L.; Desrosiers, N.; Leclerc, M.; Durocher, G. *Macromolecules* **1995**, *28*, 8587−8597. (b) Seixas de Melo, J.; Burrows, H. D.; Svensson, M.; Andersson, M. R.; Monkman, A. P. *J. Chem. Phys.* **2003**, *118*, 1550−1556.

(21) (a) Oda, M.; Meskers, S. C. J.; Nothofer, H.-G.; Scherf, U.; Neher, D. *Synth. Met.* **2000**, *111*−*112*, 575−577. (b) Oda, M.; Nothofer, H.-G.; Lieser, G.; Scherf, U.; Meskers, S. C. J.; Neher, D. *Adv. Mater.* **2000**, *12*, 362−365. (c) Oda, M.; Nothofer, H.-G.; Scherf, U.; Šunjiæ, V.; Richter, D.; Regenstein, W.; Neher, D. *Macromolecules* **2002**, *35*, 6792−6798.

(22) Coppo, P.; Schroeder, R.; Grell, M.; Turner, M. L. *Synth. Met.* **2004**, *143*, 203−206.

MA7023304