Macromolecules **2008**, *41*, 5123−5131

Influence of the Polymerization Methodology on the Regioregularity and Chiroptical Properties of Poly(alkylthiothiophene)s

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Received April 15, 2008; Revised Manuscript Received May 21, 2008

ABSTRACT: Two chiral poly(3-alkylthiothiophene)s (P3ATTs) were prepared by polymerization of 2-bromo-4-((*S*)-3,7-dimethyloctylthio)thiophene using a "modified McCullough method" (**P1**) and 2,5-dibromo-3-((*S*)-3,7-dimethyloctylthio)thiophene by the GRIM method (**P2**). **P1** was regioregular, while **P2** was regio-irregular, as confirmed by ^{1}H NMR spectroscopy. The influence of the regioregularity on the chiroptical properties was investigated and they were compared with those of HT-poly(3-alkylthiophene)s and HT-poly(3-alkoxythiophene)s. UV−vis and circular dichroism spectroscopy revealed that both polymers self-organize into chiral supramolecular aggregates upon addition of a nonsolvent and in film. Remarkably, the regioregularity has (almost) no effect on the (chiral) supramolecular organization of poly(3-alkylthiothiophene)s.

Introduction

Substituted conjugated polymers remain intensively studied materials, as they can combine processability with possibly promising electronic properties. In this respect, the substituents play a crucial role: apart from ensuring the solubility of the resulting polymers, they can also govern the eventual supramolecular structure and tune the electronic properties. For instance, λ_{max} values of head-to-tail coupled poly(3-alkylthiophene)s (HT-P3ATs)[1] and head-to-tail coupled poly(3-alkoxythiophene)s (HT-P3AOT)s[2,3] in film differ by ~120 nm.

Since a 3-substituted thiophene derivative is an asymmetric molecule, regioregularity becomes an important issue in the polymerization of these materials. The regioregularity has a tremendous influence on the properties of these polymers. Especially in the case of alkyl-substituted thiophenes, head-to-head (HH) couplings must be avoided, since they result in twists between two adjacent thiophene moieties, disrupting the conjugation.[4] Moreover, a regular molecular structure can be expected to be a requisite for good stacking, from which excellent (chir)optical and electronic properties can arise.

In principle, regioregularity in 3-substituted polythiophenes can be obtained in two ways: either by successive head-to-tail (HT) couplings or by alternating head-to-head (HH) and tail-to-tail (TT) couplings. Since HH couplings must be avoided in P3ATs, the development of regioregular P3ATs has been focusing on HT-P3ATs. Although several methodologies have been developed, the Ni-catalyzed coupling of alkyl-substituted 2-bromo-5-bromomagnesio-functionalized thiophenes constitutes their mostly used polymerization methodology.[1a,b]

In general, two major approaches for the preparation of HT coupled polythiophenes from 3-substituted thiophenes can be distinguished: either only one of the two possible isomers of the actual monomer is prepared and polymerized, or, alternatively, both isomers are prepared, but a regiospecific polymerization methodology is employed in which only one isomer of the monomer is consumed. For instance, the latter approach is applied in the GRIM methodology for the polymerization of dibromoalkylthiophenes,[1b] which consists of the in situ formation of both 3-alkyl-2-bromo-5-bromomagnesiothiophene and 4-alkyl-2-bromo-5-bromomagnesiothiophene by a Grignard metathesis reaction and subsequent polymerization using Ni(dppp)Cl_2. The reason for the regiospecificity of the catalyst is the fact that the formation of HT couplings is not promoted due to steric hindrance.[5]

Also HT coupled P3AOTs have been prepared.[2,3] Compared to HT-P3ATs, they show a significant red-shifted absorption spectrum and they are much easier oxidized. Concerning their preparation, Grignard metathesis of dibromated alkoxythiophenes again results in a mixture of both isomers,[6] but in this case, the Ni catalyst loses its regiospecificity.[2a,3] A possible explanation for this loss of regiospecificity is the fact that an oxygen atom is smaller than a methylene group. As a consequence, the synthesis of HT-P3AOT requires the use of methodologies in which only one isomer is formed. The difference in regioregularity of P3AOTs is reflected not only in, for example, their NMR spectra, but also, to a much higher extent, in properties related to their supramolecular structure, as exemplified by circular dichroism (CD) in case of chiral polymers.[3]

HT-P3ATTs, finally, have also been prepared.[7,8] Their λ_{max} is quite close to that of HT-P3ATs. The HT-P3ATTs were prepared starting from one monomeric isomer, either prepared using a Kobayashi method or by the Rieke method, which was subsequently polymerized by a Kumada or Negishi coupling reaction, respectively.

Chirality, and especially CD spectroscopy, provides a very powerful tool for the examination of the supramolecular behavior of polythiophenes.[9] For example, the difference in regioregularity in HT-P3AOTs could clearly be demonstrated by CD spectroscopy, while it was much less obvious from their UV−vis spectra.[3]

In this manuscript, it is investigated whether the GRIM methodology is also applicable for the synthesis of HT-P3ATTs. In particular, it will be examined whether the Ni-catalyst retains the regiospecificity it has for P3ATs by not promoting HT couplings due to steric hindrance. Second, the difference in (chir)optical properties of HT-P3ATTs (**P1**) and non-HT-P3ATTs (**P2**) will be studied by UV−vis and CD spectroscopy both in solution and film and compared with those of HT-P3ATs and HT-P3AOTs. See Figure 1 for structures of **P1** and **P2**.

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

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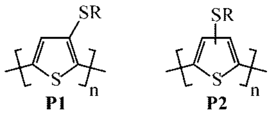


Figure 1. Structure of the polymers.

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 instrument 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 counter- and working electrode. The measurements were done in acetonitrile with Bu_4NBF_4 (0.1 M) as the supporting electrolyte under 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. 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 chloroform-solution (1500 rpm, 10 s). 3-Methoxythiophene (**1**)[10] and (*S*)-(+)-1-bromo-3,7-dimethyloctane (**7**)[11] were synthesized according to literature procedures.

Monomer Synthesis. *Synthesis of (S)-(+)-3,7-Dimethyloctanethiol (**2**).* At room temperature, thiourea (168 mmol, 12.8 g) was added to a solution of **7** (81.4 mmol, 18.0 g) in water (5 mL). After the reaction was held at reflux overnight, a solution of NaOH (160 mmol, 6.41 g) in water (50 mL) was added. The mixture was refluxed for another 2 h and then cooled to room temperature. The aqueous solution was neutralized with concentrated H_2SO_4 and extracted twice with *n*-hexane. After drying over anhydrous $MgSO_4$, the solvent was removed in vacuo and the product was isolated as a yellow liquid.

Yield: 12.5 g (88%).

$[\alpha]_D^{20} = +3.9$ deg·dm^{-1}·mol^{-1}·L ($c = 0.4$ in dichloromethane).

^{1}H NMR ($CDCl_3$): $\delta = 2.53$ (m, 2H), 1.53 (m, 4H), 1.1−1.3 (m, 6H), 0.86 (m, 9H).[12]

*Synthesis of (+)-3-((S)-3,7-Dimethyloctylthio)thiophene (**3**).* A suspension of **1** (58.0 mmol, 6.61 g), **2** (145 mmol, 11.0 g) and $NaHSO_4$ (16.6 mmol, 2.00 g) in dry toluene (10 mL) was heated overnight and methanol was distilled off. After reaction, dichloromethane was added and the mixture was successively washed with water and a saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The excess of **2** was removed by vacuum distillation and, finally, the crude product was purified by column chromatography (silica gel; eluent = petroleum ether) and isolated as a colorless oil.

Yield: 9.65 g (65%).

$[\alpha]_D^{20} = +3.4$ deg·dm^{-1}·mol^{-1}·L ($c = 2.3$ in chloroform).

^{1}H NMR ($CDCl_3$): $\delta = 7.29$ (dd, $J = 4.9$ Hz, $J = 3.0$ Hz, 1H), 7.09 (dd, $J = 3.0$ Hz, $J = 1.1$ Hz, 1H), 7.01 (dd, $J = 4.9$ Hz, $J = 1.1$ Hz, 1H), 2.82 (m, 2H), 1.52 (m, 4H), 1.1−1.3 (m, 6H), 0.87 (d, 3H), 0.85 (d, 6H).

^{13}C NMR ($CDCl_3$): $\delta = 132.6$, 129.8, 126.3, 123.0, 39.5, 37.2, 36.8, 33.4, 32.4, 28.2, 24.9, 23.0, 22.9, 19.6.

MS: $m/z = 257$ (M$^+$).

*Synthesis of (+)-2-Bromo-3-((S)-3,7-dimethyloctylthio)thiophene (**4**).* A solution of **3** (5.00 mmol, 1.28 g) in dry THF (5 mL) was shielded from light and brought under an argon atmosphere. At 0 °C, *N*-bromosuccinimide (5.25 mmol, 0.93 g) was added, and the reaction solution was allowed to warm to room temperature slowly and stirred overnight. After dilution of the solution with *n*-hexane, the organic layers were thoroughly washed with a saturated $NaHSO_3$ solution and a $NaHCO_3$ solution and dried over $MgSO_4$. The crude product was concentrated and purified by column chromatography (silica gel; eluent = petroleum ether) and isolated as a colorless oil.

Yield: 1.29 g (77%).

$[\alpha]_D^{20} = +3.2$ deg·dm^{-1}·mol^{-1}·L ($c = 2$ in chloroform).

^{1}H NMR (CD_2Cl_2): $\delta = 7.30$ (d, $J = 5.6$ Hz, 1H), 6.93 (d, $J = 5.6$ Hz, 1H), 2.86 (m, 2H), 1.4−1.6 (m, 4H), 1.1−1.3 (m, 6H), 0.87 (m, 9H).

^{13}C NMR ($CDCl_3$): $\delta = 133.5$, 130.0, 126.2, 113.0, 39.3, 37.0, 36.8, 32.9, 32.1, 28.1, 24.8, 22.7, 22.6, 19.3.

MS: $m/z = 335$ (M$^+$), 256 (M$^+$ − Br).

*Synthesis of (+)-2,5-Dibromo-3-((S)-3,7-dimethyloctylthio)-thiophene (**5**).* A solution of Br_2 (19.6 mmol, 3.13 g) in chloroform (5 mL) was added dropwise at 0 °C to a solution of **3** (9.34 mmol, 2.39 g) in chloroform (4 mL). The reaction mixture was stirred for 2 h at room temperature and then quenched with a $NaHCO_3$ solution. The mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. Finally, the product was purified by column chromatography (silica gel; eluent = petroleum ether) and isolated as a colorless oil.

Yield: 3.00 g (78%).

$[\alpha]_D^{20} = +3.8$ deg·dm^{-1}·mol^{-1}·L ($c = 0.4$ in chloroform).

^{1}H NMR ($CDCl_3$): $\delta = 6.89$ (s, 1H), 2.82 (m, 2H), 1.55 (m, 3H), 1.42 (m, 1H), 1.1−1.3 (m, 6H), 1.14 (m, 3H), 0.88 (d, 3H), 0.86 (d, 6H).

^{13}C NMR ($CDCl_3$): $\delta = 134.3$, 132.6, 113.0, 111.2, 39.5, 37.1, 36.8, 33.4, 32.2, 28.2, 24.9, 23.0, 22.9, 19.6.

MS: $m/z = 415$ (M$^+$), 334 (M$^+$ − Br).

*Synthesis (+)-2-Bromo-4-((S)-3,7-dimethyloctylthio)thiophene (**6**).* A solution of **5** (6.04 mmol, 2.50 g) in dry *n*-hexane (40 mL) was cooled to −78 °C and purged with argon. Then, *n*-BuLi (6.00 mmol, 2.40 mL, 2.50 M in *n*-hexane) was added dropwise, and the reaction mixture was stirred for 0.5 h at −78 °C. The solution was allowed to reach room temperature, and water (5 mL) was added. After the reaction mixture was diluted with diethyl ether, the organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (silica gel; eluent = petroleum ether) and isolated as a colorless oil.

Yield: 1.57 g (78%).

$[\alpha]_D^{20} = +4.2$ deg·dm^{-1}·mol^{-1}·L ($c = 2.0$ in chloroform).

^{1}H NMR ($CDCl_3$): $\delta = 7.02$ (d, $J = 1.8$ Hz, 1H), 6.88 (d, $J = 1.8$ Hz, 1H), 2.83 (m, 2H), 1.50 (m, 4H), 1.1−1.3 (m, 6H), 0.87 (m, 9H).

^{13}C NMR ($CDCl_3$): $\delta = 133.4$, 131.9, 124.2, 112.3, 39.3, 36.9, 36.4, 33.0, 32.1, 28.0, 24.7, 22.5, 22.4, 19.1.

MS: $m/z = 335.0$ (M$^+$).

Polymer Synthesis. *Synthesis of Regioregular Poly(3-((S)-3,7-dimethyloctylthio)thiophene) (**P1**).* A solution of **6** (1.79 mmol, 0.600 g) in dry THF (5 mL) was purged with argon and cooled to −78 °C. Next, a solution of LDA was added via cannula, and the reaction mixture was stirred under argon at −78 °C for 30 min and then cannulated to a suspension of anhydrous $MgBr_2$ (2.40 mmol, 5.69 mL, 0.42 M in THF). [The LDA solution was prepared by dissolving (i-Pr)$_2$NH (2.27 mmol, 0.23 g) in dry THF (5 mL). The solution was purged with argon and cooled to 0 °C. *n*-BuLi (1.95 mmol, 0.78 mL, 2.5 M in *n*-hexane) was added dropwise to the reaction mixture, which was then stirred for 30 min at room temperature.] The reaction mixture was stirred during 30 min at room temperature and finally added to a solution of Ni(dppp)Cl_2 (36.0 μmol, 18.0 mg) in dry THF (10 mL) under argon and allowed to react overnight at room temperature. The polymer solution was concentrated and poured into methanol. The precipitate was filtered off and the polymer was further purified by Soxhlet extractions using successively acetone, hexane, and chloroform. The chloroform-

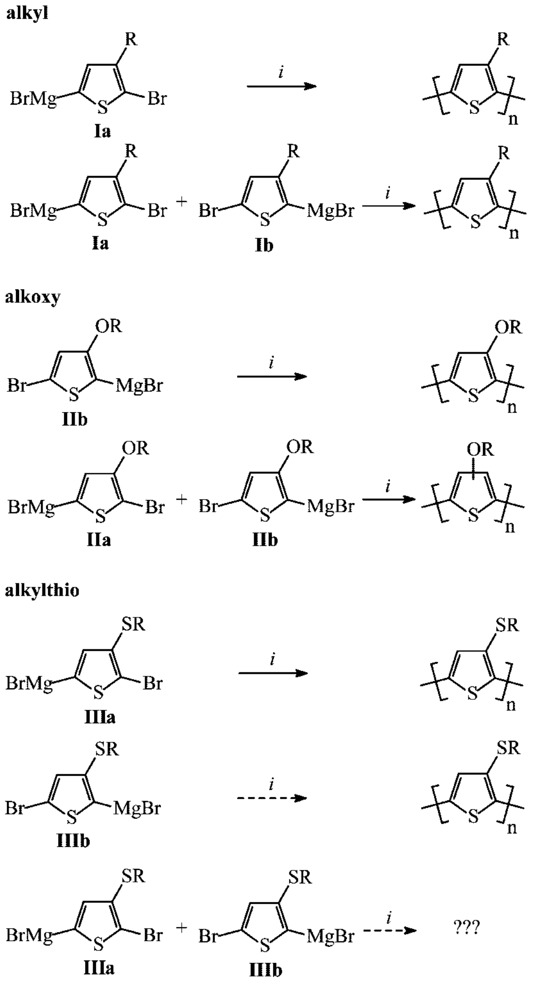


Figure 2. Comparison of the regiospecificity of the polymerization method for poly(3-alkylthiophene)s (top), poly(3-alkoxythiophene)s (middle), and poly(3-alkylthiothiophene)s (bottom). (*i*) Ni(dppp)Cl_2.

soluble fraction was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

$m = 270$ mg (59%).

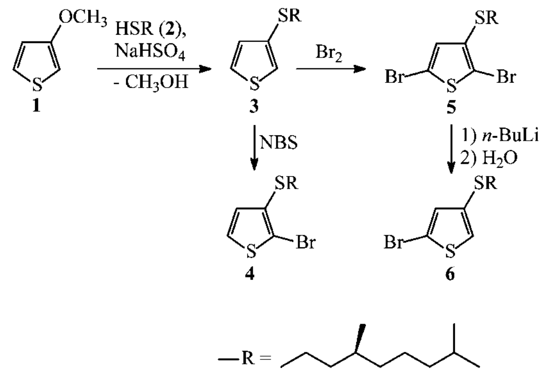
*Synthesis of Regio-Irregular Poly(3-((S)-3,7-dimethyloctylthio)-thiophene) (***P2***).* A solution of **5** (2.00 mmol, 0.83 g) in dry THF (10 mL) was purged with argon and cooled to 0 °C, and *i*-PrMgCl (2.00 mmol, 1.00 mL, 2 M in THF) was added dropwise. The reaction mixture was stirred for 30 min at 0 °C and then transferred under argon atmosphere via cannula to a solution of Ni(dppp)Cl_2 (20.0 μmol, 10.0 mg) in dry THF (10 mL). After being stirred overnight at room temperature, the polymer solution was then concentrated and poured into methanol. The precipitate was filtered off, and the polymer was further purified by Soxhlet extractions using successively acetone, hexane, and chloroform. The chloroform-soluble fraction was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

$m = 141$ mg (28%).

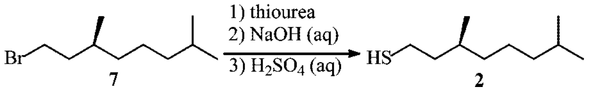
Results and Discussion

Monomer and Polymer Synthesis. A general polymerization procedure of the nickel-catalyzed polymerization of 3-alkylthiophenes is schematically shown in Figure 2, top. A first approach consists of the exclusive formation of one of the possible isomers, **Ia**, which is then polymerized using Ni(dppp)Cl_2. The actual monomer can be prepared by a McCullough procedure[1a] or by a selective Grignard metathesis reaction on 3-alkyl-2-bromo-5-iodothiophene.[5,13] In a second approach, both isomers (**Ia** and **Ib**) are prepared, as is the case in the original GRIM method[1b] or the Rieke methodology.[1e] In the Rieke method, organozinc and not organomagnesium compounds are formed. [However, their polymerization behavior seems to be analogous and, therefore, they are also withdrawn in this discussion. For the comparison of the polymerization mechanism of HT-PATTs, on the other hand, we restricted ourselves to organomagnesium compounds.] Nevertheless, the use of the proper catalyst (Ni(dppp)Cl_2) still results in HT-P3AT, because HH couplings are not promoted due to steric hindrance.[5]

Scheme 1. Synthesis of the Monomers



Scheme 2. Synthesis of the Chiral Thiol

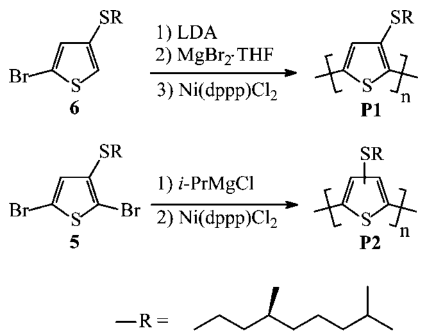


Applied on 3-alkoxythiophenes (Figure 2, middle), the GRIM method still renders a mixture of monomeric isomers. Also the McCullough method does, since scrambling of the intermediate organometallic compounds — either **IIa** or the organolithium precursor — is inevitable. An exclusive formation of one isomer of the monomers requires the synthesis of **IIb**, being the most stable one (“modified McCullough method”).[2a,3] In this way, HT-P3AOTs can be prepared, while both the McCullough and GRIM method render P3AOTs with a lower fraction of HT couplings. The reduced regiospecificity of the Ni catalyst for alkoxythiophenes compared with their alkyl counterparts can be attributed to the smaller van der Waals radius of an oxygen atom (1.5 Å) compared to a methylene group (2.0 Å), which results in less steric hindrance in case of P3AOTs.

The question now arises whether the Ni catalyst retains its regiospecificity in case of alkylthio-substituted thiophenes. In this respect, it must be mentioned that the van der Waals radius of a sulfur atom (1.8 Å) is intermediate between that of an oxygen atom and a methylene group; therefore, the steric hindrance, determining the regiospecificity, can be expected to be intermediate as well. As a consequence, in order to investigate whether the Ni-catalyst produces HT-P3ATTs starting from a mixture of isomers (**IIIa** and **IIIb**) — as is the case for P3ATs — or whether the production of HT-P3ATTs requires the formation of only one isomer (**IIIb**), analogous to P3AOTs, P3ATTs were prepared according to the GRIM and the “modified McCullough method”. The Rieke method was not chosen since, in this method, organozinc compounds are employed, undermining the comparison with the GRIM method, in which organomagnesium compounds are formed.

The synthesis of the monomers is depicted in Scheme 1. **3** was prepared using a transthioetherification reaction on **1** with the corresponding thiol. In order to be able to investigate the chiroptical properties of the resulting polymers, a chiral thiol (**2**) was used as side-chain. The synthesis of the thiol (Scheme 2) involves the reaction of **7** with thiourea and subsequent basic degradation with NaOH. To investigate the polymerization

Scheme 3. Synthesis of the Polymers



mechanism using different methodologies, several molecules were prepared. Monobromination of **3** with NBS afforded **4,** which was used for the determination of the compounds in the quenching experiments (vide infra). To prepare the monomers for the GRIM method and the "modified McCullough method", **3** was dibrominated using Br_2 to afford **5**. Treatment of **5** with *n*-BuLi in hexane and quenching with water yielded **6**.

The synthesis of the polymers is shown in Scheme 3. In a first approach, HT-P3ATT was prepared according to a "modified McCullough method", which involves the treatment of **6** with subsequently LDA, $MgBr_2 \cdot THF$ and finally $Ni(dppp)Cl_2$. In a second approach, the GRIM method was used to polymerize thioalkyl-substituted thiophenes. Therefore, **5** was treated with *i*-PrMgCl and subsequently added to the catalyst, $Ni(dppp)Cl_2$. After polymerization, all polymers were washed 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 yields of the chloroform-fraction for **P1** and **P2** are 40 and 28%, respectively. The molecular weights were determined by GPC in THF toward polystyrene standards and estimated at 9.6 kg/mol for **P1** and at 17.5 kg/mol for **P2**; the polydispersities are 1.6 and 1.4, respectively. Since the hydrodynamic volumes of the measured polymers and the standards (polystyrene) differ significantly, the determined molecular weights 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.[14]

Influence of the Polymerization Methodology on the Regioregularity. In order to investigate the regiospecificity of both polymerization methods, some quenching studies were performed during the polymerization procedure at the stage of the formation of the Grignard reagent, which is the actual monomer. Therefore, a small aliquot was withdrawn from both reaction mixtures, quenched with water and investigated by NMR (Supporting Information, Figure S1a-b). For the GRIM method, both 2-bromo-3-alkylthiothiophene and 2-bromo-4-alkylthiothiophene were recovered, indicating that two isomeric monomers (**IIIa** and **IIIb**, respectively) were formed during the reaction, as was expected for this method. The same experiment showed that, during the "modified McCullough method", only one isomer (**IIIb**) is formed and that scrambling does not occur under these conditions.

The presence of only one sharp peak in the aromatic region of the ^{1}H NMR spectrum of **P1** (Figure 3) confirms that HT-P3ATTs prepared according to the "modified McCullough method" are indeed regioregular. This is in agreement with the fact that only one isomer of the monomer is formed. The ^{1}H NMR spectrum of **P2**, on the other hand, shows more peaks in the aromatic region, demonstrating that the polymer is regio-irregular and that the GRIM method does not render regioregular P3ATTs. It must be emphasized that both NMR spectra are recorded under the same conditions (solvent, concentration) and at two different temperatures (room temperature and 50 °C). Since **P1** and **P2** have more or less an equal degree of polymerization, the difference between both can only arise from a different molecular structure and not, for instance, from differences in aggregation.

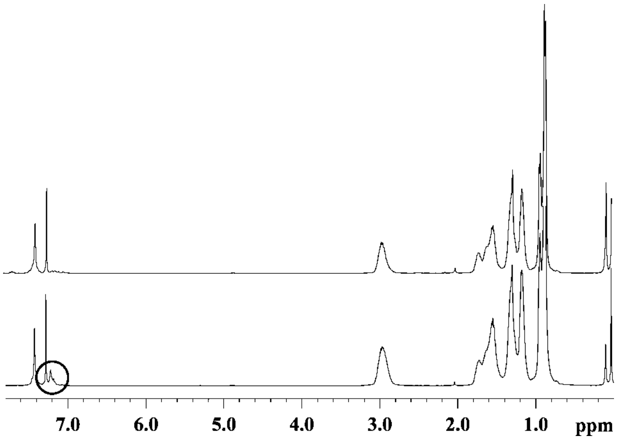


Figure 3. ^{1}H NMR spectra of **P1** (top) and **P2** (bottom) in $CDCl_3$.

Table 1. DSC and UV−Vis Data of the Polymers

			λ_{max}/nm		
polymer	T_m[a]/°C	T_c[b]/°C	chloroform	chloroform/ methanol (7/3)[c]	film[d]
P1	189	183	519	559 (611)	559 (610)
P2	186	184	510	557 (610)	557 (608)

[a] Determined by DSC at a heating rate of 20 °C/min. [b] Determined by DSC at a cooling rate of −20 °C/min. [c] Main peak (additional peak). [d] Prepared by spin coating from chloroform solution.

It can therefore be concluded that, analogous to poly(3-alkoxythiophene)s, but in contrast to poly(3-alkylthiophene)s, the production of regioregular poly(3-alkylthiothiophene)s requires the exclusive formation of only one monomeric isomer, as is the case in the "modified McCullough method" and the previously reported Kobayashi and Rieke methods.

Influence of the Regioregularity. Solubility and DSC. The regioregular **P1** is moderately soluble in $CHCl_3$ and THF. It seems to be more soluble than HT-P3ATTs substituted with linear alkylthio-substituents, which are only poorly soluble in these solvents.[8][For comparison, we also prepared HT-poly(3-octylthiothiophene) using the "modified McCullough method" and found that also for this polymer only CS_2 seems to be a good solvent, as reported by Rieke and co-workers.]

This can be attributed to the use of branched alkyl groups. The regio-irregular **P2** shows a higher solubility than **P1**, which can be explained by the presence of HH couplings, which can cause twists in the conjugated polymer backbone, thus decreasing the planarity of the polymer chains and consequently weaken the π−interactions and increase the solubility.

The observation of melting and crystallization peaks for both polymers **P1** and **P2** (Table 1) confirms their semicrystalline behavior. A glass transition was not observed. Rieke and co-workers have already shown the semicrystalline nature of achiral HT-P3ATTs by X-ray diffraction.[8] It is although remarkable that regio-irregularity, as present in **P2,** does not prevent the polymers to be semicrystalline, which is in contrast to regio-random P3ATs.[1a,e,15]

Chiroptical Properties. Representative UV−vis spectra in chloroform solution of the regioregular **P1** and regio-irregular **P2** are shown in Figure 4a,c and their λ_{max} are summarized in

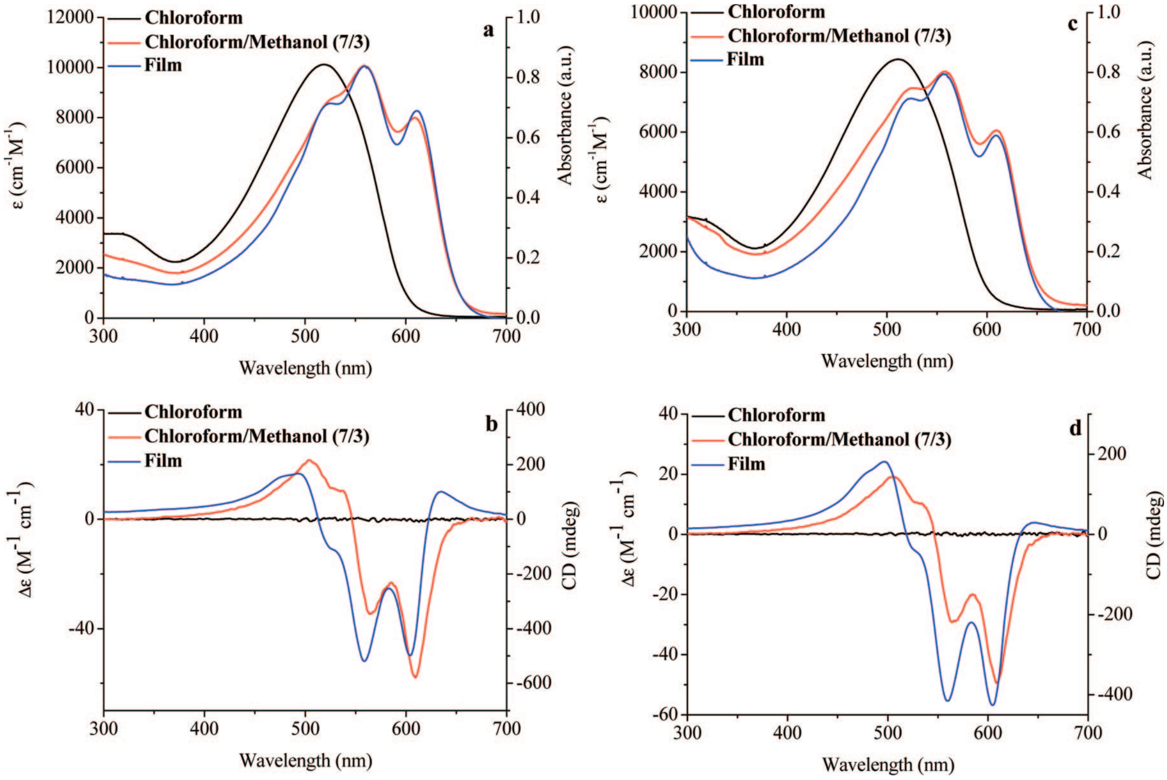


Figure 4. UV−vis (a) and CD (b) spectra of **P1** and UV−vis (c) and CD (d) spectra of **P2**.

Table 1. λ_{max} of **P1** is slightly higher than λ_{max} of other HT-P3ATTs, prepared via the Rieke method (λ_{max} = ∼504 nm[8]) and the Kobayashi method (λ_{max} = 502 nm[7]). As already stated,[8] λ_{max} of regioregular P3ATTs in good solvents lays between that of regioregular P3ATs and P3AOTs. This can be attributed to the fact that HT-P3ATs adopt a coil-like, and therefore poorly conjugated, conformation in good solvents, while S−O interactions force P3AOTs into a rod-like, strongly conjugated conformation, even in good solvents. The conformation of P3ATTs is intermediate between that of P3ATs and P3AOTs. In the case of P3AOTs, electronic effects further lower the bandgap.

The substitution pattern and regioregularity seem to have only a rather limited effect on λ_{max} of P3AOTs and P3ATTs in good solvents. It has already been shown that λ_{max} of P3AOTs and P3ATTs is slightly lower for the (regioregular) HT coupled polymers than for the (regioregular) HH-TT coupled counterparts, which was attributed to the presence of HH linkages.[16,19] This can be generalized to regio-irregular polymers as well: λ_{max} of the P3AOTs, functionalized with the same chiral dimethyloctyloxy-substituent, is 602, 583 and 590 nm (for HT[3], HH-TT,[20] and regiorandom P3AOT, prepared by the GRIM method,[3] respectively). The same tendency is observed for the P3ATTs presented here: the regiorandom **P2** displays a λ_{max} which is 9 nm lower than λ_{max} of the HT-P3ATT **P1**. Therefore, it is clear that not the regioregularity but only the amount of HH couplings determines λ_{max} of P3ATTs and P3AOTs in good solvent.

It must also be noted that no Cotton effects are observed for both polymers in chloroform (Figure 4b, d), which is in agreement with the polymer chains being rod-like and molecularly dissolved.

Upon decreasing the solvent quality, the absorption band displays a clear red-shift and a more defined fine structure. The red-shift can be attributed to an elongation of the conjugation, originating from a planarization of the backbone and subsequent stacking. The defined fine structure can be explained as vibronic fine structure, commonly observed in well-ordered systems. Interestingly, also a sharp peak, centered at 610 nm, arises. If λ_{max} of the regioregular, HT coupled **P1** (559 and 611 nm) and the regio-irregular **P2** (557 and 610 nm) are compared with those of a regioregular, HH-TT poly(3-octylthiothiophene) (552 and 601 nm),[8b] it is clear that for all polymers the distinct band near 610 nm is present. Moreover, λ_{max} of all polymers lay quite close to each other, which has been attributed to the fact that, in contrast to poly(3-alkylthiophene)s, HH couplings still allow poly(3-alkylthiothiophene)s to adopt a rather planar, transoid conformation, in which the conjugation is not disrupted. Not only does this account for the fact that λ_{max} of HT-P3ATTs and HH-TT-P3ATTs are remarkably similar,[17,18] but it also explains why λ_{max} of **P1** and **P2**, which clearly differ in the amount of HT couplings, lay very close. A similar behavior is observed for poly(3-alkoxythiophene)s.

The CD spectra show strong bisignate Cotton effects in the $\pi-\pi^*$ transition of both **P1** and **P2**; the 610 nm band, however, seems to correspond with a monosignate band. Bisignate Cotton effects with a zero-crossing at λ_{max} have been demonstrated to originate from chiral exciton coupling of chirally aligned polymer strands.[21]

In order to investigate whether the observed Cotton effects are intramolecular (chiral helical conformation of the individual polymer chains) or intermolecular (chiral supramolecular organization of different chains) in nature, the concentration dependency of both **P1** and **P2** in a chloroform/methanol mixture (85/15) was studied. For this purpose, the solvent dependency of the UV−vis and CD spectra of the polymers was first studied by varying the chloroform/methanol ratio (Supporting Information, Figure S2). Since it is clear that intermediate spectra are obtained for a chloroform/methanol (85/15) mixture, the concentration dependency was studied in this solvent mixture. From Figure 5a−d, it is clear that the observed transition for both polymers is concentration dependent, demonstrating the intermolecular nature of the process. It can therefore be concluded that both polymers are molecularly

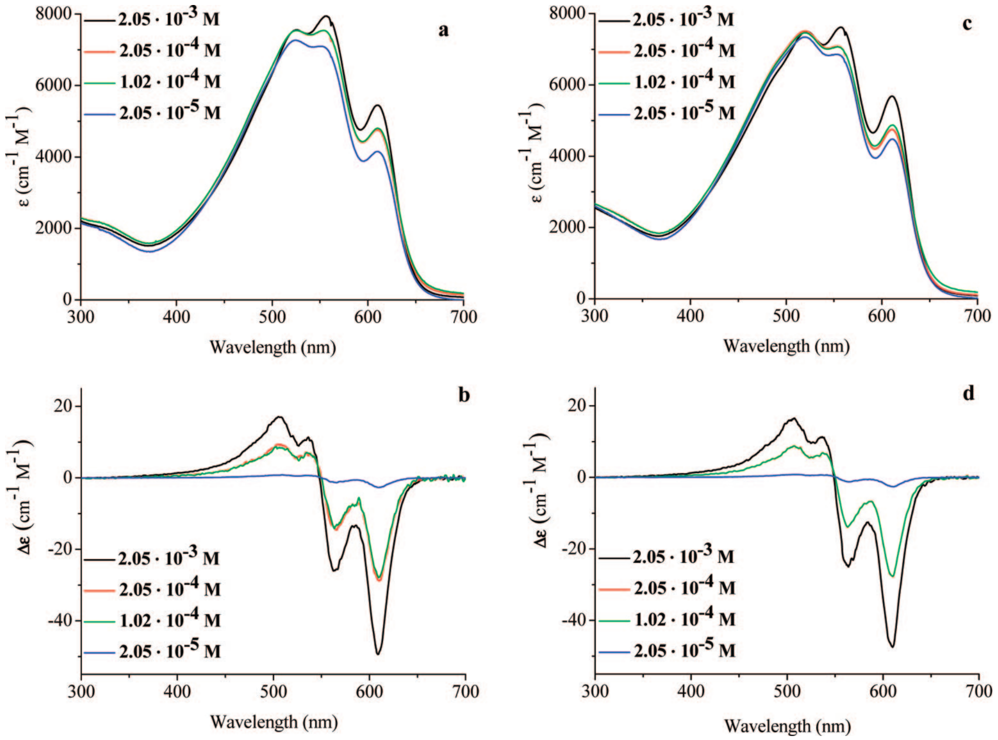


Figure 5. Concentration dependence of the UV−vis (a) and CD (b) spectra of **P1** and the UV−vis (c) and CD (d) spectra of **P2** in chloroform/methanol (85/15).

dissolved in good solvents and (chirally) aggregate upon addition of nonsolvents.

The bisignate Cotton effect near 550 nm indeed seems to correspond with the broad absorption band at 558 nm, composed of multiple vibronic bands, since the $\lambda_{\max}$ in the UV−vis spectra coincides with the zero-crossing of the CD spectra. In contrast, $\lambda_{\max}$ of the 610 nm absorption band, however, coincides very well with the *maximum* of the corresponding Cotton effect (609 nm). This becomes even more clear if the CD spectrum is compared with the derivative of the UV−vis spectrum (Supporting Information, Figure S3): the maximum of the CD does not correspond at all with the maximum of the derivative, but rather with the zero-crossing (609 nm). All these findings suggest that this Cotton effect is monosignate in nature. As a consequence, it can be concluded that the Cotton effects near 550 nm originate from chiral exciton coupling of chirally stacked polymer strands, but that the Cotton effect near 610 nm has another origin.

A sharp, red-shifted absorption band with corresponding monosignate Cotton effect has also been observed in other conjugated polymers, *i.e.*, poly(phenyleneethynylene)s (PEE),[22] HH-TT-P3AOTs, and HT-P3ATTs and HH-TT-P3ATTs. Swager and co-workers attributed this band in PEE to aggregates,[22a] while Babudri et al. proposed that it originates from strongly interacting polymer chains.[22b] From Figure 5, it is clear that this band is indeed concentration dependent and must be due to an intermolecular process. It is striking that such chiroptical behavior is only present in semicrystalline conjugated polymers. This is very nicely shown in regioregular P3AOTs: HT-P3AOT substituted with chiral dimethyloctyl groups is an amorphous material which does not show this band, while the isomeric HH-TT-P3AOT, substituted with the same groups, is semicrystalline and does display this band. Consequently, the chiroptical behavior of these polymers can be explained as follows. The broad band, situated for P3ATTs around 550 nm, arizes from coplanar, strongly conjugated polymer chains, which are chirally oriented toward each other (chiral exciton coupling); as a consequence, the corresponding Cotton effect is bisignate with a zero-crossing near $\lambda_{\max}$. This process does not require macroscopic order and is therefore present in both amorphous and semicrystalline polymers. The sharp band at lower energy, on the other hand, arises from a transition, delocalized over multiple, strongly interacting polymer chains, which are chirally ordered (in case of chiral substituents). The delocalization accounts for the red shift, while the fact that several polymer chains are involved explains the concentration dependency. Only macroscopic order makes this strong interaction possible. Finally, the fact that the actual chromophore is chiral accounts for the monosignate nature of the Cotton effect.

The chiroptical properties of **P1** and **P2** in solid state were studied in films, prepared by spincoating from a chloroform solution. After spincoating, the films were annealed, which was performed by consecutively heating them for 1 min at increasing temperatures (Supporting Information, Figure S4). An optimal annealing was accomplished at $T = 180$ °C, which can be correlated with their melting temperature (~185 °C). Annealing the films does not have a significant effect on the UV−vis spectra, but dramatically alters the CD signal. These observations demonstrate that no significant conformational changes (planarization) occur, but that rather a supramolecular reorganization of the polymer strands takes place. In that view, the observed change in the sign of the CD signal can be ascribed to changes in orientation of polymer strands with respect to each other.

After annealing, the UV−vis and CD spectra in film show great resemblances to those in a poor solvent, both in shape and g_{abs} value (for the magnitude of the g_{abs} value, see also Figure 6c,f). Therefore, the absorption bands and corresponding Cotton effects near 550 and 610 nm can tentatively be ascribed to the same processes already mentioned for the situation in poor solvent. In order to verify whether other contributions than "real" circular dichroism are present, the thickness dependency of the g_{abs} value ($= \Delta\epsilon/\epsilon$) was evaluated. Films of different thicknesses were prepared by varying the concentrations of the spin-coat solutions and all films were annealed at 180 °C. As shown in Figure 6, the g_{abs} value is thickness independent for both the 550 and 610 nm transitions of **P1** and **P2**. Therefore,

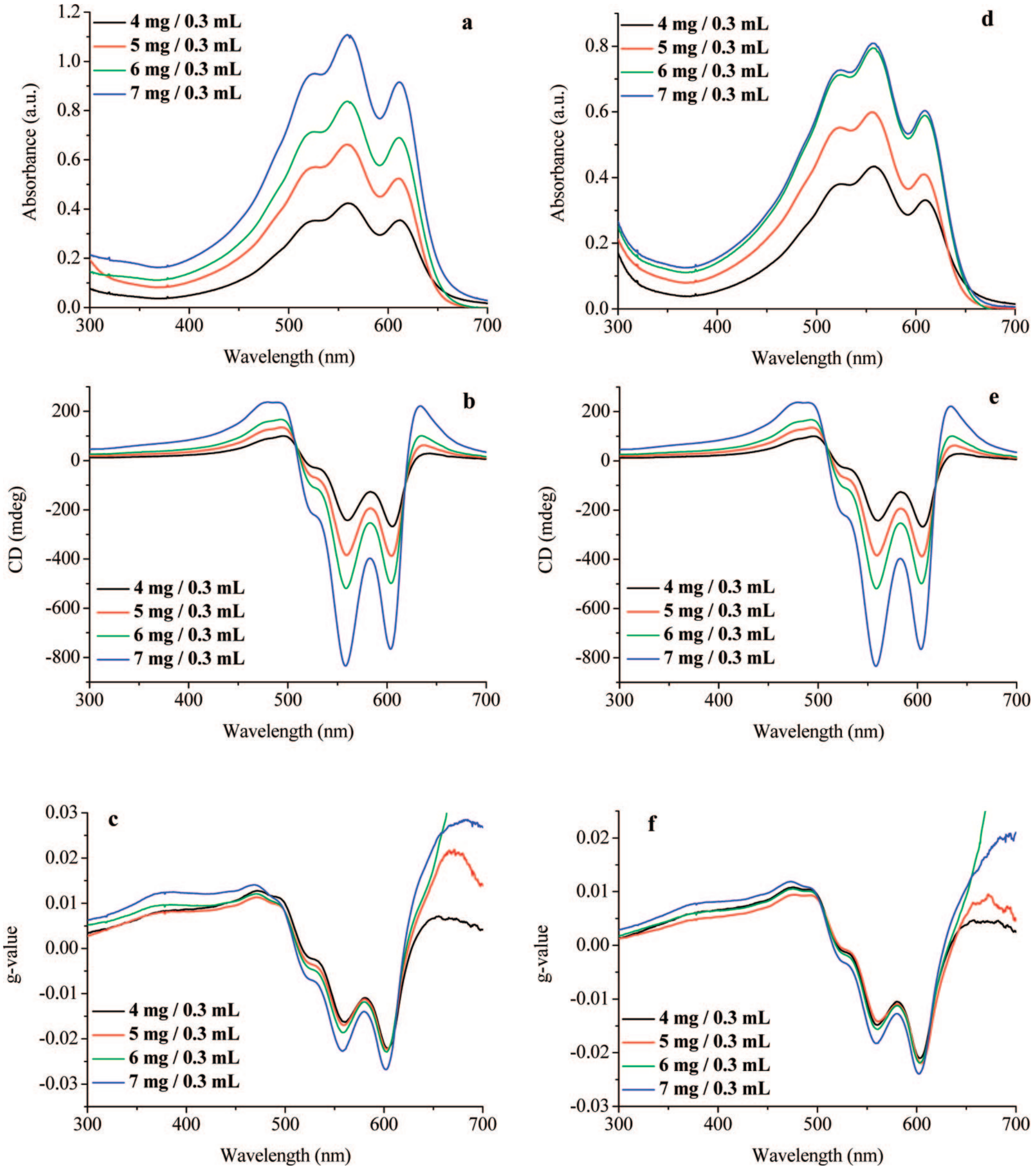


Figure 6. Thickness dependency of the UV−vis spectrum (a), CD spectrum (b) and g value (c) in film of **P1** and the UV−vis spectrum (d), CD spectrum (e), and g value (f) in film of **P2**.

these Cotton effects are due to real circular dichroism and not pseudo CD.[23] As described by Craig et al., the presence of pseudo CD would result in a thickness dependency of the g_{abs} value. Pseudo CD has been shown to be present in HT-P3AOTs,[16] but is not present in HT-P3ATs.[24]

In Figure 6b,e, an additional CD signal at 650 nm can be observed, which can be ascribed to scattering.

Remarkingly, the intensity of the CD spectra of **P1** and **P2** are quite similar, both in poor solvents and annealed films. In the annealed films, the dichroic ratio, g_{abs}, amounts 1.7×10^{-2} ($\lambda = 560$ nm) and 2.2×10^{-2} ($\lambda = 603$ nm) for the regioregular **P1**, while it is 1.6×10^{-2} ($\lambda = 560$ nm) and 2.2×10^{-2} ($\lambda = 603$ nm) for the regio-irregular **P2**. This is rather striking, since regio-irregular poly(3-alkoxythiophene)s, which are also prepared by the GRIM methodology, show a g_{abs} value which is 1 order of magnitude lower than that of their regioregular HT coupled[3] and HH-TT coupled[20] counterparts. That significantly lower g_{abs} value reflects the difficulty of regio-irregular P3AOTs to (chirally) stack, although being planar, which probably results from its irregular molecular structure. Regioregularity and even stereoregularity have been shown to influence the supramolecular organization of poly(3-alkylthiophene)s and other conjugated polymers, such as poly(phenylenevinylene)s[25] and poly(3,4-dialkoxythiophene)s.[26] The chiral poly(3-alkylthiothiophene)s, however, still maintain their ability to stack chirally, regardless of being regioregular or not. Although it is not clear at this moment why regio-irregular poly(3-alkylthiothiophene)s display significant supramolecular chirality while their corresponding regio-irregular poly(3-alkoxythiophene)s do not, it must be noted that this might be correlated with the fact that both **P1** and **P2** are semicrystalline, which is not the case for their HT coupled alkoxy-substituted counterparts.

Emission Spectroscopy. Solution fluorescence data were obtained for both polymers in chloroform solution and are summarized in Table 2. Both polymers show the same emission wavelength (616 nm), demonstrating that their excited state, in which the conjugated system is present in its quinoidal form, is electronically equal. Therefore, these findings are consistent with the fact that P3ATT can adopt a planar conformation, even if HH couplings are present. The ground state, on the other hand, is influenced by the presence of HH linkages - $\lambda_{\max}$ of **P2** is (slightly) lower than **P1**. As a consequence, the Stokes shift of **P2** is slightly larger than that of **P1**.

Table 2. Emission Data of the Polymers

	in chloroform				in chloroform/methanol (7/3) (c = 15 mg/L)			
polymer	λ_{ex}/nm	λ_{em}/nm	fwhm$_{em}$^{a}/cm^{-1}	Stokes shift/cm^{-1}	λ_{ex}/nm	λ_{em}/nm	fwhm$_{em}$^{a}/cm^{-1}	Stokes shift/cm^{-1}
P1	500	616	1393	3034	560	644	1225	2393
P2	500	616	1428	3354	560	649	1324	2545

[a] Full width at half-maximum of the emission band.

If the Stokes shifts and broadness of the emission peak of the HT-P3ATTs are compared with those of HT-P3ATs (4385 and 2738 cm^{-1})[1e] and HT-P3AOTs (494 and 1541 cm^{-1})[20], more or less intermediate values are found for HT-P3ATTs, confirming that the conformation is intermediate of HT-P3AT and HT-P3AOT.

If the polymers are aggregated, the fluorescence dramatically drops. Consistent with the increased rigidity present in the aggregates, the broadness of the emission peak and the Stokes shift decreases. Finally, the intensity of the fluorescence is concentration-dependent (Supporting Information, Figure S5), which confirms the supramolecular nature of the solvent-induced process.

Electrochemical Behavior. 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 by cyclic voltammetry (Supporting Information, Figure S6a-b). E_{pa} and E_{pc} were typically determined from the second scan. The oxidation process of both polymers is quasi-reversible and the half-wave potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$) of **P1** and **P2** are identical (1.01 V), again demonstrating that both polymers have the same conjugation length and are equally well planarized in film. The HOMO levels can be calculated at −5.24 eV.[27]

If the electrochemical properties of **P1** are compared with those of HT-P3AT and HT-P3AOT, substituted with the same dimethyloctyl group (Supporting Information, Figure S6c), it can be concluded that the S-atom does not significantly influences the electronic properties of the polythiophene backbone. In this respect, HT-P3ATTs rather resemble HT-P3AT than HT-P3AOT.[8]

Conclusion

In conclusion, two chiral poly(3-alkylthiothiophene)s were prepared using a “modified McCullough” and a GRIM method. The influence of the regiospecificity of both methodologies was investigated. It was found that the Ni-catalyst employed (Ni(dppp)Cl$_2$) requires the exclusive formation of only one isomer of the actual monomer to prepare regioregular polymers. As a consequence, the “modified McCullough method” produces regioregular HT-P3ATTs, while the GRIM method does not. Regio-irregular HT-P3ATTs are slightly less conjugated in solution than regioregular HT-P3ATTs, but in poor solvents and films, both polymers planarize and stack and equal conjugation lengths are observed, reflecting the possibility of P3ATTs to adopt a coplanar conformation around a HT coupling. Remarkably, both polymers show almost identical CD spectra, indicating that the chiral stacking is not influenced by regio-irregularity. The UV−vis spectra in poor solvents are a superposition of the π-π* transition of the polymer chains and a sharp, red-shifted band. In the CD spectra, a bisignate Cotton effect is observed in the π−π* transition, arising from chiral exciton coupling, while the red-shifted band corresponds with a monosignate Cotton effect. This band can tentatively be ascribed to a transition, delocalized over the chiral aggregate.

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 Number FA8655-07-1-3004 for financial support. K.V.d.B. is a doctoral fellow of the IWT and G.K. is a postdoctoral fellow of the Fund for Scientific Research (FWO-Vlaanderen).

Supporting Information Available: Figures showing quenching studies on the monomer formation, the influence of the chloroform/methanol ratio on UV−vis and CD spectra of **P1** and **P2**, a comparison of the CD spectra and the derivative of the UV−vis spectra, UV−vis and CD spectra in film at different annealing temperatures, concentration dependence of the emission, CV spectra of the polymers and a comparison with HT-P3ATs and HT-P3AOTs, 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.

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MA8008405