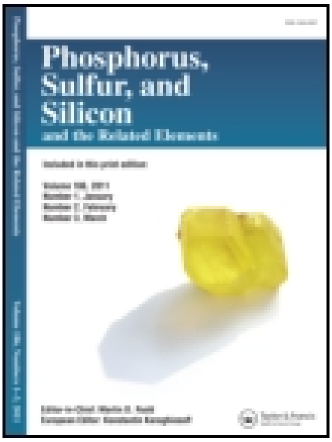

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The Chemo- and Electropolymerization of Thiophene Derivatives Containing at the Third Position of A Substituent with A Stereogenic Phosphorus Atom

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THE CHEMO- AND ELECTROPOLYMERIZATION OF THIOPHENE DERIVATIVES CONTAINING AT THE THIRD POSITION OF A SUBSTITUENT WITH A STEREOGENIC PHOSPHORUS ATOM

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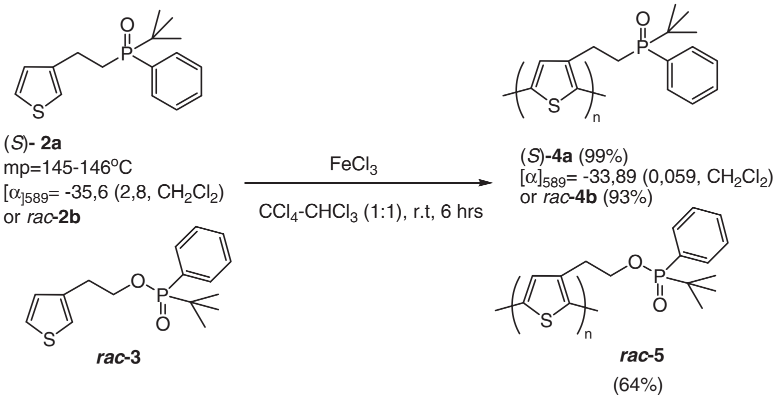
GRAPHICAL ABSTRACT



Abstract *Recently, differently functionalized polythiophenes (PTs) have found a broad application in material chemistry. Now, we are working in our laboratories on the synthesis of such derivatives functionalized at the third postion of a thiophene ring with a substituent containing a stereogenic heteroatom. In this paper, we would like to report our preliminary results devoted to the chemo- and electropolymerizations of monomeric thiophene derivatives. The classical three-electrode system used for electropolymerization carried out on platinum (Pt), glassy carbon (GC), and gold (Au) electrodes in acetonitrile with lithium perchlorate as the supporting electrolyte electrolyte will be presented. The chemical polymerization was based on the oxidative coupling using ferric chloride, leading to high molecular weight products.*

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Keywords Chiral polythiophene derivatives; oxidative coupling; chemical polymerization; fluorescent properties; random regioisomerism

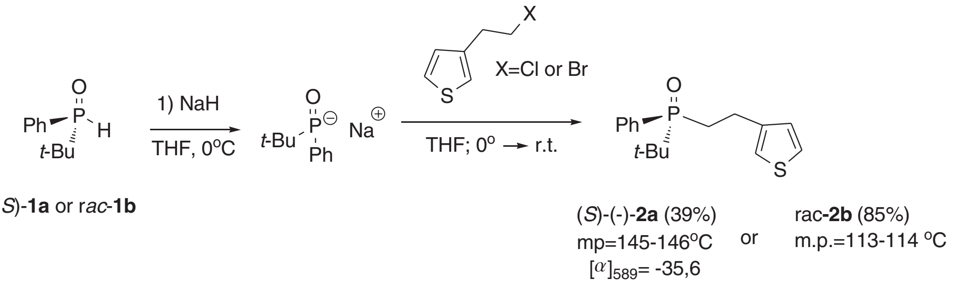
INTRODUCTION

Among the number of π-conjugated polymers, substituted polythiophenes (PTs) are one of the most important and widely studied conductive materials that can be used in a variety of application for field-effect transistors, polymer light-emitting diodes, antistatic coatings, batteries, electromagnetic shielding materials, solar cells, or bio- or gas sensors.[1] Functionalization of an aromatic backbone by a side chain allows an easier processing of such polymeric materials, but most importantly promotes their electronic properties. Recently, a lot of efforts have been devoted to the preparation of chiral PTs functionalized with a substituent containing a stereogenic carbon atom, for example, in amino alcohols, amino acids, esters, and ethers. It is reasonable to expect that they should show optical activity when the polymer chains adopt a suitably ordered conformation (or self-assembled aggregates) in slightly polar solvents, at low temperatures or in a solid state.[2,3]

Selected functionalized chiral PTs have already found practical applications, for example, as good candidates for the preparation of enantioselective electrodes, membranes, electroactive chiral surface, optically active catalysts, or optically active chromatographic support.[4,5] Below we are going to describe part of our recent experiments devoted to the synthesis and basic structural determinations of new chiral PT systems functionalized at the third position of a thiophene ring with a substituent containing a stereogenic heteroatom.

Synthesis of Monomers

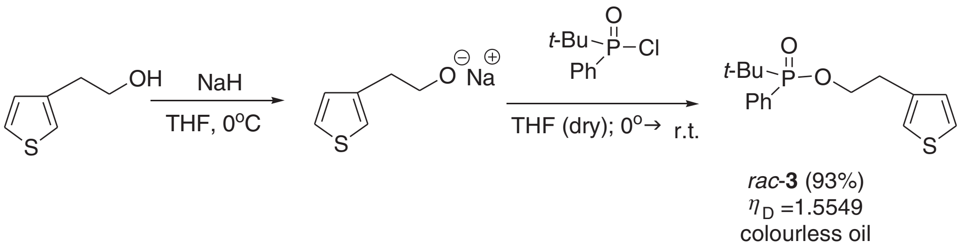
Enantiomerically pure and racemic *tert*-butylphenylphosphine oxides [(*S*)-**1a** or *rac*-**1b**] were synthesized following the known procedure.[6] Racemic and enantiomerically pure (*S*)-*tert*-butylphenyl-2-(3′-thiophene)ethyl phosphine oxides **2a,b** were obtained by the patented procedure[7] *via* alkylation of the metallated oxides **1a** (generated by a direct deprotonation of oxide with sodium hydride in THF at 0°C) with 2-(3′-thienyl)ethyl bromide(chloride). The reaction proceeds with the retention of the configuration at a phosphinyl phosphorus atom, giving the expected oxide **2a** without detectable racemization (Scheme 1).



Scheme 1

Its enantiomeric purity (higher than 99%) was established by NMR spectroscopy using (*S*)–(–) –*tert*–butylphenylphosphinothioic acid as a chiral solvating agent (CSA).

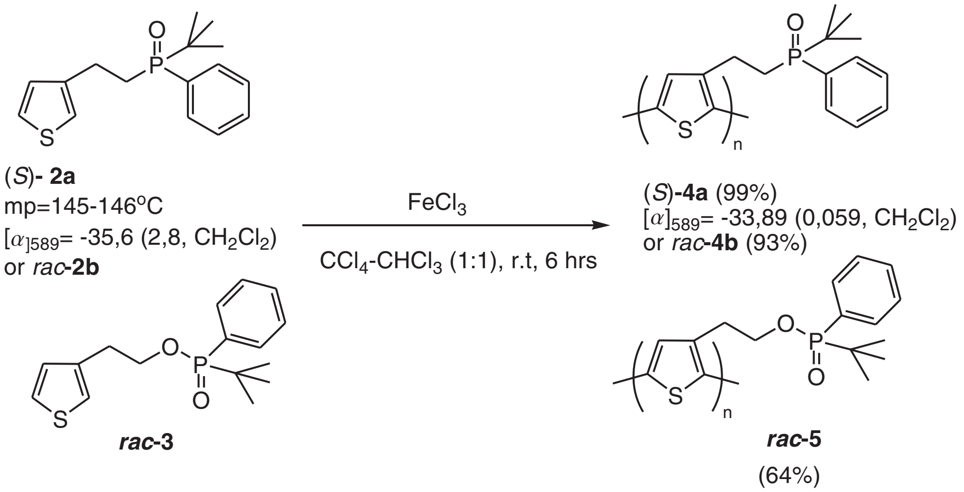
Racemic *O*-2-(3′-thienyl)ethyl *tert*-butylphenylphosphinate **3** was prepared in 93% yield by the reaction of sodium 2-(3′-thienyl)ethoxide with *tert*-butylphenylposhinyl chloride (Scheme 2).



Scheme 2

Chemical Polymerization

The 3-substituted PTs were synthesized by a modification of standard chemical polymerization based on an oxidative coupling with iron trichloride as oxidative agent.[8] Our optimal reaction condition for polymerization are based on the use of a mixture of $CCl_4/CHCl_3$ as a reaction medium (Scheme 3). The resulting polymers were obtained in good yield as orange solids and were identified by spectroscopic methods. Racemic polyphosphinic ester **5** was additionally purified by a Soxhlet extraction with methanol.



Scheme 3

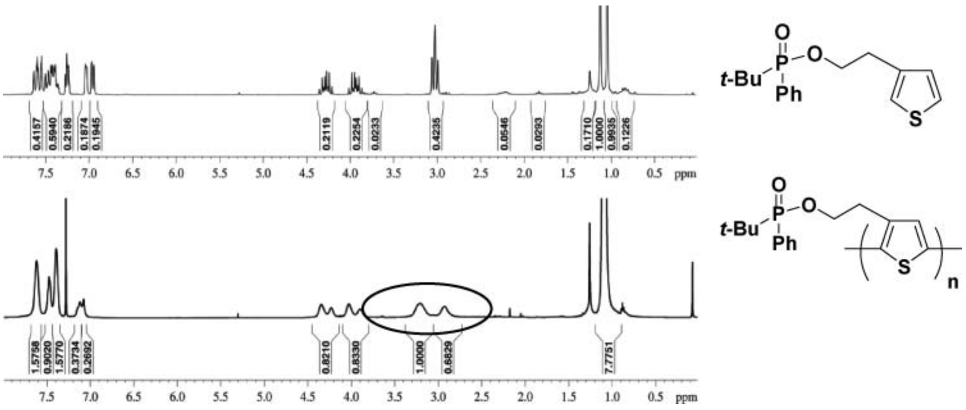


Figure 1 ^{1}H NMR spectra of O-2-(3′-thienyl)ethyl tert-butylphenylphosphinate and its polymeric analog in $CDCl_3$.

Physicochemical and Structural Characterization of Polymeric Derivatives

The isolated polymeric products **4** and **5** are soluble in dichloromethane, chloroform, and tetrahydrofuran. Their good solubility should allow an easier processing and potential application as conductive materials. The structures of the isolated polymeric samples were confirmed by NMR spectroscopy. ^{1}H-NMR spectra clearly confirmed the presence of α,α‘-conjugated thiophene system having an irregular structure as can be expected for the chemical polymerization induced by $FeCl_3$. This conclusion is based on the presence in the ^{1}H NMR spectrum of polymeric *O*-2-(3′-thiophene)ethyl *tert*-butylphenylphosphinate recorded in $CDCl_3$ of two resonance peaks (in the range of 2.93 to 3.21 ppm) assigned to the methylene protons of the CH_2 group bonded directly with the thiophene rings (Figure 1). They indicate the presence of HT and HH (or TT) coupling chains. The HT coupling percentage in the main chain can be approximately calculated from the ratio of the intensities of signals of the α-methylene protons. The regioregularity of PT **5** measured

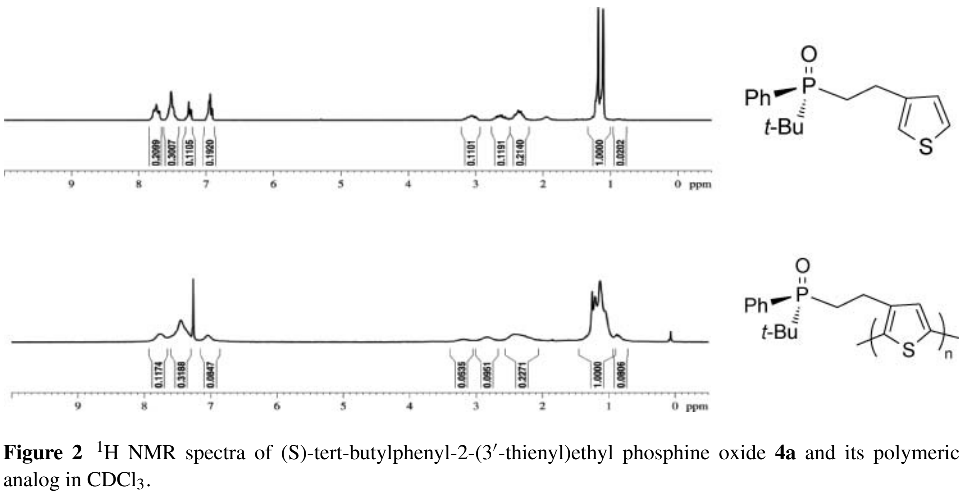


Figure 2 ^{1}H NMR spectra of (S)-tert-butylphenyl-2-(3′-thienyl)ethyl phosphine oxide **4a** and its polymeric analog in $CDCl_3$.

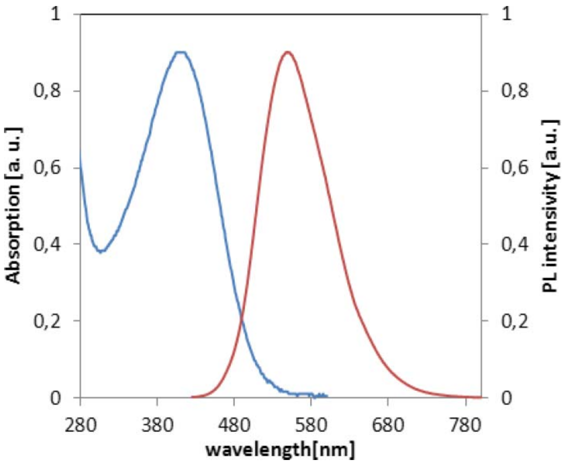


Figure 3 Absorption and emission spectra of **(S)-4a** in $CHCl_3$ ($C = 3 \times 10^{-5}$ M), λexc = 411 nm (Color figure available online).

by the head-to-tail content is equal to ca 59%. In the case of the polymeric material derived from (*S*)- *tert*-butylphenyl-2-(3′-thiophene)ethyl phosphine oxide **4a**, determination of the degree of regioregularity from the ^1H NMR spectrum is more difficult. However, it is evident from the analysis of peak intensities of all the CH_2 proton groups that the isolated PT derivative contains, in fact, the HH or TT defects (Figure 2.).

Optical Properties of Polymers (*S*)-4a and 5. UV-Visable Aborption and Fluorescence

The optical properties of the dedoped polymers **4a** and **5** were examined as chloroform solutions by UV-visible and fluorescence spectroscopy. They exhibit the characteristic band originating from the π-conjugated polymer backbone with a maximum of absorption at 411 and 420 nm, respectively. These bands can be attributed to a coil conformation of the main PT chain. The UV-VIS absorption maxima for both polymers are blue-shifted, reflecting a decrease in effective conjugation length. This is consistent with random regioisomerism of the measured samples. Moreover, photoluminescence spectra of (*S*)-**4a** and **5** showed a maximum emission at 549 nm indicating a yellow fluorescence (Figs. 3, 4).

No	Solvent	λmax (A) [nm]	ν_A [cm^{-1}]	λmax (F) [nm]	ν_F[cm^{-1}]	Stokes Shift [cm^{-1}]
4a	$CHCl_3$	411	24331	549	18215	6116
5	$CHCl_3$	420	23810	549	18215	5595

Electrochemical Studies

To characterize the electrochemical properties of isolated thiophenes **2b** and **3** the cyclic voltammetric method was used. Both monomers were oxidized at a potential between 1.16 V (on Au electrode) and at +0.6 V up to +1.95 V vs. Ag/AgCl (on platinum [Pt]

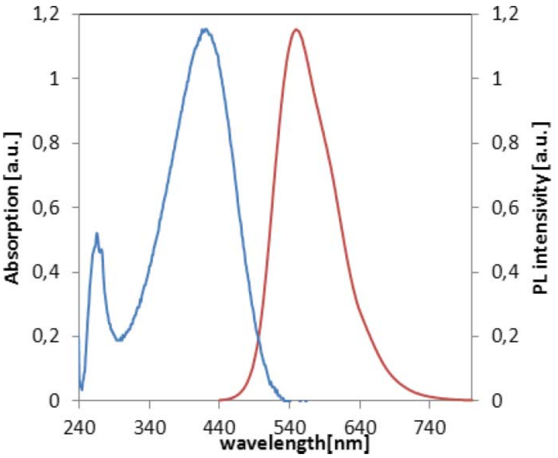


Figure 4 Absorption and emission spectra of **rac-5** in $CHCl_3$ ($C = 1{,}6 \times 10^{-5}$ M), $\lambda exc = 420$ nm (Color figure available online).

electrode). The cyclic voltammograms showed three types of behavior.[9] The peaks height of compound **3** decreases and the cyclic voltammogram approximates the base line in the cycles thereafter. No reduction peaks were obtained at a studied potential range. From the decreasing current it was concluded that a thin nonconductive film was deposited on the surface of the electrode (Fig. 6). The racemic phosphine oxide **2b** showed another characteristic behavior on gold (Au) and glassy carbon (GC) electrodes. The oxidation current decreased after the first cycle but increased in the cycles thereafter. These results mean that no deposition of a redoxidizable polymer films on the electrodes surfaces were observed. The resulting polymer formed a colloidal greenish glow at the bottom of the cell. **2b** Showed on a Pt electrode another different behavior (Fig. 5). The cyclic voltammograms of this system showed a little decreasing of the oxidation current in contrast to the case for **3**. This result is not clear and requires further study.

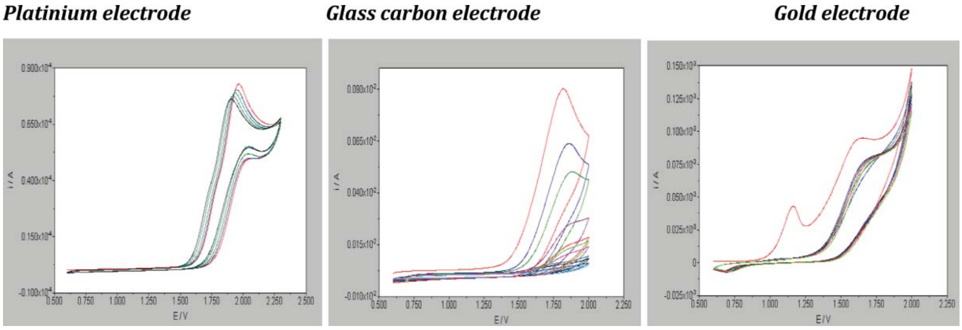

Platinium electrode ***Glass carbon electrode*** ***Gold electrode***

Figure 5 Cyclic voltammograms of polymerization of tert-butylphenyl-2-(3′-thienyl)ethyl phosphine oxide **rac-2b** in $CH_3CN + LiClO_4$ on Pt, Gc, and Au electrodes, respectively. Repetitive sweeps between 0.6–2 V vs. Ag/AgCl electrode. The red lines indicate the 1st scan (Color figure available online).

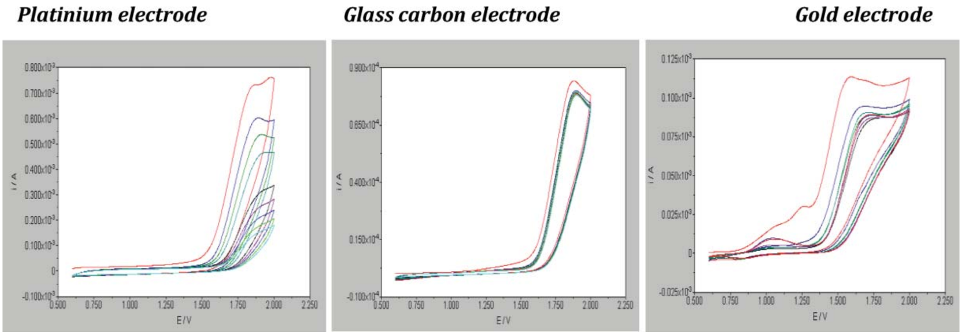


Figure 6 Cyclic voltammograms of polymerization of O-2-(3′-thienyl)ethyl tert-butylphenylphosphinate **rac 3** in $CH_3CN + LiClO_4$ on Pt, Gc, and Au electrodes, respectively. Repetitive sweeps between 0.6–2 V vs. Ag/AgCl electrode. The red lines indicate the 1st scan (Color figure available online).

Experimental

The NMR spectra were recorded on a Bruker spectrometer Avance AV 200 (Bruker, Karlsruhe, Germany) (200.16 MHz (^{1}H), 50.30 MHz (^{13}C), 81,03 MHz (^{31}P)) in $CDCl_3$. Mass spectral data were collected on MAT95-Finnigan spectrometer (Finnigan MAT, Bremen, Germany). Optical rotation was determined on 241 MC-Perkin Elmer polarimeter (Perkin Elmer,Vienna, Austria) at room temperature. Melting point was determined on Betius apparatus (PHMK VEB Analytik, Dresden, Germany) and was uncorrected. Tetrahydrofuran (THF) and diethyl ether were dried and distilled over sodium in the presence of benzophenone under argon atmosphere. $CHCl_3$ was purified by distillation over P_2O_5. CH_2Cl_2 was dried with CaH_2 before use. The reactions were carried out under dry argon. Column chromatography was performed on Merk Silica Gel (F_{254} 60, 270–400 mesh). Merk Silica F254 plates were used for thin layer chromatography and visualization was effected with UV light (254 nm). UV/Vis absorption spectra were recorded at room temperature with resolution increment 1 nm using a Nicolet Evolution 300 spectrophotometer. The fluorescence spectra were recorded at room temperature with resolution increment 1 nm, slit 3 using a FluoroMax-4 spectrophotometer. The source of light was a 150 W continuous ozone-free xenon lamp. IR spectra were recorded as KBr pellets using FT IR 60 instrument. ATI Mattson, Mass spectral data were collected on a MAT95–Finnigan spectrometer (Finnigan MAT, Bremen, Germany). Microanalyses were performed with a CHNSO-EA1108 analyzer.

The electropolymerization of thiophene derivatives has been studied with cyclic voltammetry. Potential sweeps were controlled by a AUTOLAB PGSTAT 128N potentiostat/galvanostat (Metrohm Autolab B.V., Utrecht, Netherlands). The measurements were carried out in typical three-electrode system: a platinum gauze as the counter electrode, Ag/AgCl electrode as reference and Pt, GC, or Au electrodes as the working ones. The experiments were conducted in 0.1 M solutions of lithium perchlorate as the supporting electrolyte in acetonitrile. The solution was deareated for 15 min. by dry argon bubbling and electropolymerization took place under argon atmosphere. The measurements have been recordered with the potential scan rate of 50 mV/s at 298 K. Potentials were cycled between +0.6 V and +2.0 V or +2.25 V vs. the Ag/AgCl electrode. The concentration of thiophenes that were examined were 0.01 mol L-1.

TERT-BUTYLPHENYL-2-(3′-THIENYL)ETHYL PHOSPHINE OXIDE–racemic Mixture. To a stirred suspension of 50%-NaH (0.763 g, 15.90 mmol) in THF (50 mL) at 0°C under argon atmosphere secondary *tert*-butylphenylphosphine oxide **1b** (2.633 g, 14.45 mmol) dissolved in THF (50 mL) was slowly dropped. After stirring at 0°C for 1 h, freshly distilled 2-(3′- thienyl)ethyl chloride (2.120 g, 14.45 mmol) was added to the reaction mixture. The reaction mixture was stirred at 0°C for 3 h, and then was allowed to reach room temperature and stirred at RT for additional 21 h. The reaction was monitored by ^{31} P NMR spectroscopy. After 24 h, when the presence of substrate was not observed, the reaction mixture was treated with 50 mL of saturated ammonium chloride solution and extracted with 50 mL CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The crude product (3.690 g) was purified by washing with cold hexane to give 3.584 g (yield 84.9%) of *tert*-butylphenyl-2-(3′-thiophene)ethyl phosphine oxide as a white solid. mp = 113°C –114°C

^{1}H NMR [ppm] (200 MHz, $CDCl_3$) $\delta = 1.14$ (d, $^{3}J_{P\text{-}H} = 14.50$ Hz, 9H, Me_3C), 2.23–2.43 (m, 2H, CH_{2}.-$C3'_{Tiof}$), 2.48–2.72 (m, 1H, CH_2–P), 2.97–3.16 (m, 1H, CH_2–P), 6.91–6.95 (m, 2H, Ar_{Tiof}), 7.21–7.24 (m, 1H, Ar_{Tiof}), 7.45–7.58 (m, 3H, Ar), 7.69–7.78 (m, 2H, Ar);

^{31}P NMR [ppm] (81 MHz, $CDCl_3$) $\delta = 48.93$;

^{13}C NMR [ppm] (50 MHz, $CDCl_3$) $\delta = 20.99$ (d, $J = 3.22$ Hz, $\underline{C}H_2$–$C3'_{Tiof}$), 23.05 (d, $J = 62.02$ Hz, $\underline{C}H_2$–P), 23.19 (s, $(\underline{C}H_3)_3C$), 31.46 (d, $J = 68.90$ Hz, $CH_3\underline{C}$), 119.30 (s, C2’ $_{Tiof}$), 124.52 (s, C5’ $_{Tiof}$), 126.50 (s, C4’ $_{Tiof}$), 127.03 (d, $J = 10.56$ Hz, *o*-C_{Ar}x2), 128.51 (d, $J = 86.05$ Hz, *ipso*-C_{Ar}), 130.19 (s, *p*-C_{Ar}), 130.56 (d, $J = 7.8$ Hz, *m*-C_{Ar}x2), 140.62 (d, $J = 14.44$ Hz, C3′ $_{Tiof}$).

MS (CI/izobutan): *m/z* (%): 293.2 (100) [M + 1], 585.3 (72,5) [2M + 1].

HRMS (EI) dla $C_{16}H_{21}OPS$: calcd.: 292.10507, found: 292.10488.

Elem. Anal. for $C_{16}H_{21}OPS$: calcd.: C (65.73%), H (7.24%), S(10.97%); found: C (65.82%), H (7.08%), S (10.95%).

IR (KBr) [ν/cm^{-1}]: 3074; 3048 (C–H_{aryl}); 2979; 2933; 2911; 2865 (C–H_{alif}); 1464, 1435; 1169; 1156 (s) (P=O).

TERT-BUTYLPHENYL-2-(3′-THIENYL)ETHYL PHOSPHINE OXIDE-optically Active Form. To a stirred suspension of 50%-NaH (0.082g, 1.71 mmol) in THF (5 mL) at 0°C under argon atmosphere dissolved in tetrahydrofuran (10 mL) secondary (*S*)-*tert*-butylphenylphosphine oxide (0.282g, 1.55 mmol) was slowly dropped. After stirring at 0°C for 1 h, freshly distilled 2-(3′- thienyl)ethyl bromide (0.296 g, 1.55 mmol)) was added to the reaction mixture. The reaction mixture was stirred at 0°C for 3 h, and then was allowed to reach room temperature and stirred for the next 24 h. The reaction was monitored by ^{31} P NMR spectroscopy. After 27 h, when the presence of substrate was not observed, the reaction mixture was treated with 15 mL of saturated ammonium chloride solution and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were washed with brine and dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The crude product (0.439 g) was purified by crystallization from CH_2Cl_2: hexane solution to give 0.176 g (yield: 39%) of enantiomarically pure (*S*)-*tert*-butylphenyl-2-(3′-thienyl)ethyl phosphine oxide as white solid.

$[\alpha]_D = -35{,}57$ (2,8, CH_2Cl_2)

mp = 145–146°C

^{1}H NMR [ppm] (200 MHz, $CDCl_3$) $\delta = 1.15$ (d, $^3J_{P\text{-}H} = 14.47$ Hz, 9H, Me_3C), 2.23–2.49 (m, 2H, CH_2-$C3'_{Tiof}$), 2.54–2.72 (m, 1H, CH_2–P), 2.97–3.16 (m, 1H, CH_2–P), 6.91–6.95 (m, 2H, Ar_{Tiof}), 7.21–7.24 (m, 1H, Ar_{Tiof}), 7.49–7.52 (m, 3H, Ar), 7.70–7.78 (m, 2H, Ar);

^{31}P NMR [ppm] (81 MHz, $CDCl_3$) $\delta = 48.92$;

MS (CI/isobutane): *m/z* (%): 293.2 (100) [M+1], 585.3 (72.5) [2M+1]

Elemental analysis: dla $C_{16}H_{21}OPS$: calcd.: C(65.73%), H (7.24%), S (10.97%); found: C (65.64%), H (7.11%), S (10.99%);

IR (KBr) [ν/cm^{-1}]: 3075, 3049 (C–H_{aryl}); 2979; 2933; 2912; 2866 (C–H_{alif}), 1464; 1435; 1169; 1156 (s) (P = O).

O-2-(3′-THIENYL)ETHYL TERT-BUTYLPHENYLPHOSPHINATE rac-3. To a stirred suspension of 50%-NaH (0.824g, 34.32 mmol, 1.1 equiv) in THF (20 mL) at 0°C under argon atmosphere 3-thiopheneethanol (2 g, 15.6 mmol) was added. After stirring at 0°C for 2 h, a solution of *tert*-butylphenylphosphinyl chloride (3.337g, 15.36 mmol) in THF (10 mL) was added to the reaction mixture. The reaction was monitored by ^{31} P NMR spectroscopy. After 6 h the reaction mixture was treated with 30 mL of saturated ammonium chloride solution and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine and dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The product (4.474 g) was obtained in 93% yield as colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.09 (d, $J = 15.67$ Hz, 9H, $(C\underline{H}_3)_3C$); 3.03 (t, $J = 6.66$ Hz, 2H, $C\underline{H_2}$–Tiof); 3.87–3.98 (m, 1H, $C\underline{H_2}$–O–P); 4.02–4.35 (m, 1H, $C\underline{H_2}$–O–P); 6.96 (dd, $J = 0.84$; 4.66 Hz, 1H, Tiof); 7.04 (d, $J = 1.84$ Hz; 1H, Tiof); 7.24–7.28 (m, 1H, Tiof); 7.35–7.65 (m, 5 H, Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ 24.04 ($(\underline{C}H_3)_3C$); 31.46 (d, $J = 6.7$ Hz; $\underline{C}H_2$–O–P); 32.44 (d, $J = 100.4$ Hz, $(CH_3)_3\underline{C}$); 64.43 (d, $J = 7.2$ Hz, $\underline{C}H_2$–Tiof); 121.77; 125.41; 127.45; 128.16 (d, $J = 11.56$ Hz, C_{orto} × 2); 128.36; 131.94 (d, $J = 2.49$ Hz); 133.03 (d, $J = 8.86$ Hz, C_{meta} × 2); 137.91.

^{31} P NMR (81 MHz, $CDCl_3$): δ 51.51(s).

MS (CI/isobutane): *m/z*:111; 309 [M + 1].

HRMS (EI) dla $C_{16}H_{21}O_2PS$: calcd.: 308.0996, found: 308.0999.

Chemical Polymerization

General procedure: Iron trichloride (4 equiv) was suspended in a $CHCl_3/CCl_4$ (1:1) mixture (c = 0.08 M). The studied monomer was dissolved in $CHCl_3/CCl_4$ (1:1) (c = 0.08 M) and the solution was added dropwise to the reaction mixture at room temperature under argon atmosphere. The mixture was stirred for 6 h under a flow of argon. The reaction mixture was treated with 1M HCl and diluted with $CHCl_3$. The organic phase was washed with HCl solution untill the Fe(III) ions were present in the inorganic phase. The chloroform phase was dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent gave the crude polymers. The polyester **5** was additionally purified by a Soxhlet extraction with methanol.

POLYMER 4a

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.13–1.21 (bm, 9H, $C(CH_3)_3$), 2.42 (bm, 2H, CH_2); 2.83, 2.19 (2bm, 2H, CH_2); 7.04 (bm, 1H, 4-Thioph); 7.45, 7.76 (2bm, 5 H, Ph);

^{31} P NMR (81 MHz, $CDCl_3$): δ 48.75 49.12 (bm)

POLYMER 4b

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.12 (bm, 9H, $C(CH_3)_3$), 2.38, 2.83, 3.16 (3xbm, 4H, $2 \times CH_2$); 7.00 (bs, 1H), 7.44, 7.71 (2 × bm, 5 H, Ph).

^{31} P NMR (81 MHz, $CDCl_3$): δ 48.93 (bm)

POLYMER 5

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08–1.10 (bm, 9H, $C(CH_3)_3$), 2.92, 3.21 (2 × bm, 2H, CH_2); 3.99, 4.03, 4.23, 4.35 (4 × bm, 2H, CH_2–OP); 7.08, 7.12 (2 × bm, 1H); 7.40, 7.47, 7.62 (3 × bm, 5 H, Ph)

^{31} P NMR (81 MHz, $CDCl_3$): δ 52.86 (bm)

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