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Influence of the Substituent and Polymerization Methodology on the Properties of Chiral Poly(dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s

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ABSTRACT: New poly(*N*-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s (PDTPs) with high molecular weights, good yields, and increased solubility were prepared, and their supramolecular behavior was studied. The polymers differ in their polymerization method (using chemical oxidants, Stille-couplings, or a Yamamoto-type polymerization) and the bulkiness of the side chain. The solubility of the polymer depends on the bulkiness of the side chains employed, while the yield and, to a lesser extent, the molecular weight depend on the polymerization method. In general, Stille-couplings proved to be the best polymerization method for PDTPs. The higher molecular weight polymers showed more defined voltammograms, higher λ_{max} together with the presence of a vibronic fine-structure, and higher fluorescence yields than lower molecular weight materials. In solution, the polymers are present as highly conjugated rigid rods, which, upon transition to films or in nonsolvents, poorly aggregate. The stacking is more complicated in high molecular weight polymers than in low molecular weight samples.

Introduction

In our quest for the synthesis and study of chiral, soluble conjugated polymers with a stable oxidized state, we became particularly interested in poly(*N*-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s (PDTPs). PDTPs are highly conjugated polymers, which, in comparison with regioregular poly(3-alkylthiophene)s, show reduced bandgaps and a very stable oxidized state.[1−3]

The first synthesis of (achiral) PDTPs includes an electrochemical polymerization of DTP monomers.[1] These materials were highly conjugated and could easily be oxidized but lacked solubility. Next, *N*-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole monomers were polymerized with a chemical oxidant.[2,3] These polymers were typically substituted with a linear or slightly branched alkyl group. Unfortunately, the polymers appeared to be low molecular weight materials ($\bar{M}_n \sim 1-4$ kg/mol, 5−10 repeating units), and depending on the experimental conditions,[3] only low to moderate yields were obtained. Probably, only the low molecular weight fractions were soluble. However, it has been proposed that increasing the degree of polymerization can enhance the (optical) properties of the materials.[3]

We rationalized that there are two possible reasons for the poor solubility and low molecular weight of the polymers and the low yields. The first one is the nature of the polymerization process (oxidatively), in which the polymers are prepared in their oxidized, less soluble state. Moreover, some cross-linking cannot be excluded. These problems can be circumvented by the use of organometallic-catalyzed reactions, in which the polymers are grown in their neutral form in a fashion, determined by the substitution pattern of the functional groups on the monomers. A second reason can be the π-stacking between the polymer backbones, which is probably too strong in the polymers. The use of bulky groups would reduce the π-stacking and therefore increase the solubility.

In this paper, we further derivatize PDTPs in order to increase the yields, solubility, and molecular weights. The influence on the electrochemical and (chir)optical properties will be discussed. Finally, also the supramolecular structure of PDTPs in films and solution will be proposed.

Experimental Section

Reagents and Instrumentation. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, and Avocado. Reagent grade solvents were dried when necessary 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 AVIV 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 an argon atmosphere. Ferrocene was added before each run as an internal standard. The Fe(II/III) couple of ferrocene was observed at 0.460 V (scan rate = 50 mV/s). For the measurements, a polymer film was dropcasted 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.[4] 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).

1[5] and (*S*)-1-bromo-3,7-dimethyloctane[6] were synthesized according to literature procedures.

Synthesis of the Amines. Synthesis of (*R*)-(−)-2-Amino-1-(octyloxy)butane (6c). Under an argon atmosphere, a solution of **2** (20.0 mL, 211 mmol) in dry DMF (40 mL) was added dropwise to a suspension of NaH (5.06 g, 211 mmol) in dry DMF (30 mL). Then, a solution of 1-bromooctane (36.7 mL, 211 mmol) in dry DMF (40 mL) and a small amount of NaI were added to the mixture. The reaction mixture was stirred for 24 h at 60 °C under an argon atmosphere, after which it was cooled and poured into

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ice water (300 mL). The crude compound was extracted three times with diethyl ether. The combined organic layers were washed with a saturated $NaHCO_3$ solution and with brine, dried over $MgSO_4$, and concentrated in vacuo. After vacuum distillation, the amine was isolated as a viscous, colorless oil. Yield: 5.65 g (13%); bp: 87 °C/ 0.75 mmHg. $[\alpha]_D^{20} = -3.6$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 3.41$ (m, 3H), 3.14 (t, 1H), 2.86 (qu, 1H), 1.57 (m, 2H), 1.2−1.5 (m, 14H), 0.94 (t, 3H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 76.1$, 71.3, 52.4, 31.8, 29.7, 29.4, 29.2, 27.1, 26.2, 22.6, 14.0, 10.4. MS: $m/z = 201.6$ (M^+) (calcd: 201.4).

Synthesis of 9-Aminoheptadecane (6d). Synthesis of 1-Octylnonanol (4d). A solution of ethyl formate (9.26 g, 125 mmol) in dry diethyl ether (20 mL) was added dropwise to a freshly prepared solution of octylmagnesium bromide [obtained by adding a solution of 1-bromooctane (48.3 g, 250 mmol) in dry diethyl ether (75 mL) to a suspension of Mg (6.08 g, 250 mmol) in dry diethyl ether (50 mL)] at such a rate that gentle reflux was maintained (10−15 min). After addition, stirring was continued for 10 min, and H_2O (18 mL) was added at such a rate that rapid refluxing occurred. This was followed by addition of a mixture of concentrated sulfuric acid (7.75 mL) in H_2O (67.5 mL). The solids were filtered off and thoroughly washed with diethyl ether. The combined organic layers were washed three times with a saturated $NaHCO_3$ solution and brine. After drying over $MgSO_4$, the solvents were removed in vacuo. Finally, the product was purified by recrystallization from acetonitrile. Yield: 26.7 g (83%); mp: 59−60 °C. ^1H NMR ($CDCl_3$): $\delta = 3.59$ (m, 1H), 1.2−1.5 (m, 29H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 72.2$, 37.6, 32.0, 29.9, 29.7, 29.4, 25.8, 22.8, 14.3. MS: $m/z = 256.4$ (M^+) (calcd: 256.5).

Synthesis of *N*-[1-Octylnonyl]phthalimide (5d). A solution of triphenylphosphine (13.1 g, 50.0 mmol), phthalimide (7.36 g, 50.0 mmol), and **4d** (12.8 g, 50.0 mmol) in dry diethyl ether (50 mL) was purged with argon, and a solution of DIAD (9.70 mL, 50.0 mmol) in dry diethyl ether (20 mL) was slowly added. After stirring overnight, the precipitate was filtered off and washed thoroughly with diethyl ether. After removal of the solvent via rotary evaporation, the crude compound was purified by column chromatography (silica gel; eluent: dichloromethane/hexanes 10/90 (v/v)) and isolated as a colorless oil. Yield: 11.5 g (60%). ^1H NMR ($CDCl_3$): $\delta = 7.82$ (dd, $J = 5.5$ Hz, $J = 2.7$ Hz, 2H), 7.70 (dd, $J = 5.5$ Hz, $J = 2.7$ Hz, 2H), 4.19 (m, 1H), 2.07 (m, 2H), 1.70 (m, 2H), 1.1−1.4 (m, 24H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 168.9$, 133.9, 132.0, 123.2, 52.5, 32.6, 31.9, 29.5, 29.4, 29.3, 26.8, 22.8, 14.2. MS: $m/z = 385.6$ (M^+) (calcd: 385.6), 255.4 ($M^+ - C_8H_2O_2$).

Synthesis of 9-Aminoheptadecane (6d). A solution of **5d** (7.94 g, 20.6 mmol) in absolute ethanol (40 mL) was purged with argon, and hydrazine monohydrate (1.00 mL, 20.6 mmol) was added dropwise. The mixture was heated to reflux for 2 h. Then, excess HCl solution (5 M) was added, and the mixture was refluxed for an additional 10 min and cooled. The precipitate was filtered off and washed with water. The filtrate was concentrated in vacuo, and excess NaOH solution (2 M) was added. The crude compound was extracted twice with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvents were removed via rotary evaporation. The amine was isolated as a viscous, colorless oil by vacuum distillation. Yield: 3.07 g (58%); bp: 127 °C/ 0.5 mmHg. ^1H NMR ($CDCl_3$): $\delta = 2.66$ (m, 1H), 1.2−1.5 (m, 28H), 1.10 (s, 2H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 51.3$, 38.3, 32.0, 29.9, 29.7, 29.4, 26.3, 22.7, 14.1. MS: $m/z = 255.5$ (M^+) (calcd: 255.6).

Synthesis of (6*S*,12*S*)-(−)-9-Amino-2,6,12,16-tetramethylheptadecane (6e). Synthesis of (4*S*,3′*S*)-(−)-1-(3′,7′-Dimethyloctyl)-4,8-dimethylnonanol (4e). The same procedure was followed as described for the synthesis of **4d**, starting from (*S*)-1-bromo-3,7-dimethyloctane. The crude compound was purified by column chromatography (silicagel; eluent: dichloromethane/hexanes 50/50 (v/v)) and isolated as a colorless oil. Yield: 22.7 g (58%). $[\alpha]_D^{20} = -3.1$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 3.53$ (m, 1H), 1.0−1.6 (m, 25H), 0.87 (d, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 72.9$, 39.5, 37.4, 35.0, 33.0, 33.0, 28.1, 24.9, 22.8, 19.8. MS: $m/z = 312.7$ (M^+) (calcd: 312.6).

Synthesis of (4*S*,3′*S*)-(−)-*N*-[1-(3′,7′-Dimethyloctyl)-4,8-dimethylnonyl]phthalimide (5e). The same procedure was followed as described for the synthesis of **5d**, starting from **4e**. The product was isolated as a colorless oil. Yield: 11.9 g (54%). $[\alpha]_D^{20} = -2.4$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 7.82$ (dd, $J = 5.5$ Hz, $J = 2.7$ Hz, 2H), 7.70 (dd, $J = 5.5$ Hz, $J = 2.7$ Hz, 2H), 4.12 (m, 1H), 1.9−2.2 (m, 2H), 1.6−1.8 (m, 2H), 0.9−1.5 (m, 20H), 0.7−0.9 (m, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 168.9$, 133.9, 132.0, 123.2, 53.1, 39.4, 37.2, 34.0, 32.7, 30.2, 28.1, 24.9, 22.8, 19.8. MS: $m/z = 441.6$ (M^+) (calcd: 441.8), 311.6 ($M^+ - C_8H_2O_2$).

Synthesis of (6*S*,12*S*)-(−)-9-Amino-2,6,12,16-tetramethylheptadecane (6e). The same procedure was followed as described for the synthesis of **6d**, starting from **5e**. The product was isolated as a viscous, colorless oil after vacuum distillation. Yield: 3.50 g (55%); bp: 170 °C/ 2.3 mmHg. $[\alpha]_D^{20} = -4.2$ deg dm^{-1} mol^{-1} L ($c = 0.7$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 2.62$ (m, 1H), 1.0−1.6 (m, 26H), 0.87 (d, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 52.1$, 39.4, 37.4, 35.7, 33.6, 33.1, 28.1, 24.9, 22.8, 19.8. MS: $m/z = 311.6$ (M^+) (calcd: 311.7).

Synthesis of the Monomers. A general procedure for the synthesis of *N*-functionalized dithieno[3,2-*b*;2′,3′-*d*]pyrroles (**7a**−**e**) is as follows:[7] A solution of **1** (2.00 g, 6.18 mmol), NaO*t*Bu (1.42 g, 14.8 mmol), Pd_2dba_3 (0.142 g, 0.155 mmol), and BINAP (0.386 g, 0.620 mmol) in dry toluene (12 mL) was purged with argon for 20 min. The appropriate amine (6.18 mmol) was added via syringe, and the mixture was stirred at 110 °C under an argon atmosphere until completion of the reaction (TLC analysis, takes about 7 h). After cooling, water was added and the layers were separated. The water phase was extracted twice with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvents were removed via rotary evaporation. Finally, the crude compound was purified by column chromatography.

***N*-Octyldithieno[3,2-*b*:2′,3′-*d*]pyrrole (7a).**[1a] The crude compound was purified by column chromatography (silica gel; eluent: hexanes/dichloromethane 90/10 (v/v)) and isolated as yellow crystals. Yield: 80%; mp: 34.9−35.4 °C. ^1H NMR ($CDCl_3$): $\delta = 7.12$ (d, $J = 5.5$ Hz, 2H), 7.00 (d, $J = 5.5$ Hz, 2H), 4.19 (t, 2H), 1.86 (qu, 2H), 1.2−1.4 (m, 10H), 0.86 (t, 3H).

Synthesis of *N*-Cyclododecyldithieno[3,2-*b*:2′,3′-*d*]pyrrole (7b). The crude compound was purified by column chromatography (silica gel; eluent: hexanes) and isolated as yellow crystals. Yield: 32%; mp: 158−160 °C. ^1H NMR ($CDCl_3$): $\delta = 7.11$ (d, $J = 5.9$ Hz, 2H), 7.05 (d, $J = 5.9$ Hz, 2H), 4.52 (qu, 1H), 2.1−2.2 (m, 2H), 1.8−1.9 (m, 2H), 1.3−1.6 (m, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 144.2$, 122.5, 114.9, 112.0, 54.5, 30.6, 29.9, 24.2, 24.1, 22.9, 22.8. MS: $m/z = 345.4$ (M^+) (calcd: 345.6).

(*R*)-(−)-*N*-[1-(Octyloxymethyl)propyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (7c). The crude compound was purified by column chromatography (silica gel; eluent: hexanes/dichloromethane 50/50 (v/v)) and isolated as a dark oil. Yield: 77%. $[\alpha]_D^{20} = -1.5$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 7.07$ (d, $J = 5.0$ Hz, 2H), 7.03 (d, $J = 5.0$ Hz, 2H), 4.34 (qu, 1H), 3.76 (d, 2H), 3.2−3.4 (m, 2H), 2.05 (qu, 2H), 1.44 (m, 2H), 1.1−1.3 (m, 10H), 0.88 (t, 3H), 0.80 (t, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 144.4$, 122.3, 115.1, 112.1, 72.7, 71.5, 61.0, 31.8, 29.6, 29.4, 29.3, 26.0, 24.3, 22.7, 14.2, 11.0. MS: $m/z = 363.4$ (M^+) (calcd: 363.6).

***N*-(1-Octylnonyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole (7d).** The crude compound was purified by column chromatography (silica gel; eluent: hexanes) and isolated as a colorless solid. Yield: 71%; mp: 59−60 °C. ^1H NMR ($CDCl_3$): $\delta = 7.10$ (d, $J = 5.5$ Hz, 2H), 7.01 (d, $J = 5.5$ Hz, 2H), 4.21 (m, 1H), 2.00 (m, 2H), 1.82 (m, 2H), 1.0−1.4 (m, 24H), 0.84 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 144.2$, 122.5, 114.9, 111.9, 59.9, 35.3, 31.9, 29.4, 29.3, 26.7, 22.8, 14.2. MS: $m/z = 417.5$ (M^+) (calcd: 417.8).

(4*S*,3′*S*)-(−)-*N*-[1-(3′,7′-Dimethyloctyl)-4,8-dimethylnonyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (7e). The crude compound was purified by column chromatography (silica gel; eluent: hexanes) and isolated as a colorless oil. Yield: 76%. $[\alpha]_D^{20} = -1.5$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^1H NMR ($CDCl_3$): $\delta = 7.10$

(d, $J = 5.5$ Hz, 2H), 7.01 (d, $J = 5.5$ Hz, 2H), 4.14 (m, 1H), 1.7−2.1 (m, 4H), 0.9−1.5 (m, 20H), 0.83 (d, 6H), 0.80 (d, 6H), 0.78 (d, 3H), 0.76 (d, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 144.2$, 122.5, 114.9, 111.9, 60.6, 39.3, 37.0, 33.8, 32.8, 32.5, 28.1, 24.8, 22.8, 19.7. MS: $m/z = 473.7$ (M^+) (calcd: 473.9).

Synthesis of 2,6-Diiodo-*N*-(1-octylnonyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole (8d). At 0 °C and under an argon atmosphere, *t*-BuLi (2.80 mL, 4.20 mmol, 1.5 M in pentane) was cannulated to a solution of **7d** (0.836 g, 2.00 mmol) in dry diethyl ether (100 mL). After the reaction was stirred for 1 h at room temperature, a solution of I_2 (1.27 g, 5.00 mmol) in dry diethyl ether (10 mL) was added dropwise via syringe. After stirring for another 2 h, the mixture was transferred into a separatory funnel and was successively washed with a $Na_2S_2O_3$ solution, a $NaHCO_3$ solution, and brine. The organic layer was dried over $MgSO_4$, and the solvent was removed via rotary evaporation. Finally, the crude compound was purified by column chromatography (silica gel; eluent: dichloromethane/hexanes 90/10 (v/v)) and by recrystallization from acetonitrile and isolated as white crystals. Yield: 0.92 g (69%); mp: 77.5−78.5 °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.16$ (s, 2H), 4.07 (m, 1H), 1.91 (m, 2H), 1.79 (m, 2H), 0.9−1.3 (m, 24H), 0.86 (t, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 143.0$, 121.1, 119.4, 70.5, 60.3, 35.1, 31.9, 29.4, 29.3, 26.6, 22.8, 14.3. MS: $m/z = 669.1$ (M^+) (calcd: 669.6), 542.4 ($M^+ - I$).

Synthesis of (4S,3′S)-(−)-2,6-Diiodo-*N*-[1-(3′,7′-dimethyloctyl)-4,8-dimethylnonyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (8e). The same procedure was followed as described for **8d**, starting from **7e** (4.50 g, 9.50 mmol). The crude compound was purified by column chromatography (silica gel; eluent: petroleumether) and isolated as a dark oil. Yield: 4.62 g (67%). $[\alpha]_D^{20} = -3.2$ deg dm^{-1} mol^{-1} L ($c = 1$ in chloroform). ^{1}H NMR ($CDCl_3$): $\delta = 7.16$ (s, 2H), 3.99 (m, 1H), 1.84 (m, 4H), 1.46 (m, 2H), 1.26 (m, 4H) 0.9−1.2 (m, 14H), 0.80 (d, 12H), 0.77 (d, 6H). ^{13}C NMR ($CDCl_3$): $\delta =$ 143.0, 121.1, 119.5, 70.5, 61.0, 39.3, 37.0, 33.8, 32.8, 32.3, 28.1, 24.8, 22.8, 19.8. MS: $m/z = 725.2$ (M^+) (calcd: 725.7), 598.6 ($M^+ - I$).

Synthesis of 2,6-Di(trimethyltin)-*N*-(1-octylnonyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole (9d). At 0 °C and under an argon atmosphere, *t*-BuLi (2.10 mL, 3.15 mmol, 1.5 M in pentane) was cannulated to a solution of **7d** (0.627 g, 1.50 mmol) in dry diethyl ether (70 mL). The reaction was stirred for 1 h at room temperature, and a solution of Me_3SnCl (0.678 g, 3.40 mmol) in dry diethyl ether (10 mL) was added dropwise via syringe. After stirring for another 2 h at room temperature, the solution was concentrated in vacuo. The crude compound was dissolved in hexanes, and the precipitate was filtered off. The solvent was removed via rotary evaporation, leaving a dark green, viscous oil, which was used without further purification. Yield: 1.05 g (94%). ^{1}H NMR ($CDCl_3$): $\delta = 6.98$ (s, 2H), 4.22 (m, 1H), 2.02 (m, 2H), 1.82 (m, 2H), 1.0−1.4 (m, 24 H), 0.84 (t, 6H), 0.39 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta = 147.2$, 135.1, 120.4, 118.9, 59.7, 35.2, 32.0, 29.5, 29.4, 26.7, 22.8, 14.3, −8.0. MS: $m/z = 743.5$ (M^+) (calcd 743.4), 417.5 ($M^+ - C_6H_{18}Sn_2$).

Synthesis of (4*S*,3′*S*)-(−)-2,6-Di(trimethyltin)-*N*-[1-(3′,7′-dimethyloctyl)-4,8-dimethylnonyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (9e). The same procedure was followed as described for the synthesis of **9d**, starting from **7e**. The product was isolated as a dark green, viscous oil and was used without further purification. Yield: 1.16 g (97%). $[\alpha]_D^{20} = -2.8$ deg dm^{-1} mol^{-1} mL ($c = 2$ in chloroform). ^{1}H NMR ($CDCl_3$): $\delta = 6.99$ (s, 2H), 4.15 (m, 1H), 1.7−2.1 (m, 4H), 0.6−1.5 (m, 38H), 0.39 (s, 18H). ^{13}C NMR ($CDCl_3$): $\delta =$ 147.3, 135.2, 120.5, 118.9, 60.4, 39.4, 37.1, 33.9, 32.9, 32.6, 28.1, 24.8, 22.8, 19.7, −8.0. MS: $m/z = 799.6$ (M^+) (calcd: 799.5), 474.6 ($M^+ - C_6H_{18}Sn_2$).

Synthesis of the Polymers. Oxidative Polymerization (P*-ox). A general procedure is as follows: A suspension of anhydrous $RuCl_3$ (0.823 g, 4.00 mmol, weighed in a drybox) in dry chloroform (10 mL) was purged with argon. An argon-purged solution of the dithienopyrrole monomer **7** (1.00 mmol) in dry chloroform (5 mL) was added via cannula to the suspension under an argon atmosphere. The polymerization reaction was vigorously stirred at room temperature under a light argon flow for 2 h. The mixture was stirred overnight at 60 °C and poured into methanol. The precipitate was filtered off and boiled in a mixture of THF/$N_2H_4 \cdot H_2O$ (90/10 (v/v)) for 2 h. The solvents were removed via rotary evaporation, and the polymer was precipitated into methanol. The precipitate was filtered off, and the polymer was further purified by Soxhlet extractions using successively acetone, hexanes, and chloroform. The chloroform-soluble fraction (or hexanes-soluble fraction in the case of **Pe-ox**) was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

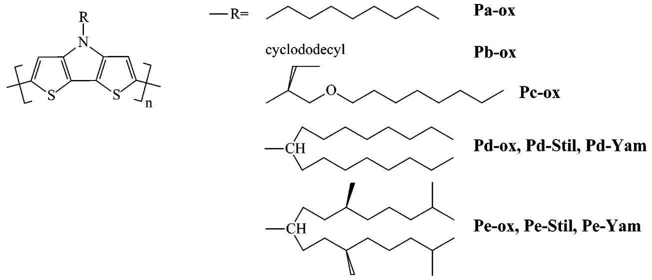


Figure 1. Structure of the polymers.

Yamamoto-Type Polymerization (P*-Yam). A general procedure is as follows: $Ni(COD)_2$ (0.303 g, 1.10 mmol, weighed in a drybox), COD (0.123 mL, 1.00 mmol), and 2,2′-bipyridine (0.172 g, 1.10 mmol) were dissolved in dry, argon-purged DMF (3 mL). The solution was heated at 80 °C for 0.5 h, and an argon-purged solution of the dithienopyrrole monomer **7** (0.500 mmol) in dry toluene (3 mL) was added via syringe. The reaction was maintained at 80 °C for 96 h in the dark. After cooling, an aqueous solution of HCl (1 mL, 4 M) was added to quench the polymerization. The mixture was diluted with chloroform, transferred into a separatory funnel, and washed successively with an aqueous HCl (2 M) solution, with a saturated EDTA solution, with a saturated $NaHCO_3$ solution, and with brine. The combined organic layers were dried over Na_2SO_4, subsequently concentrated, and finally precipitated into methanol. The polymer was further purified by Soxhlet extractions using successively acetone, hexanes, and chloroform. The chloroform-soluble fraction was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

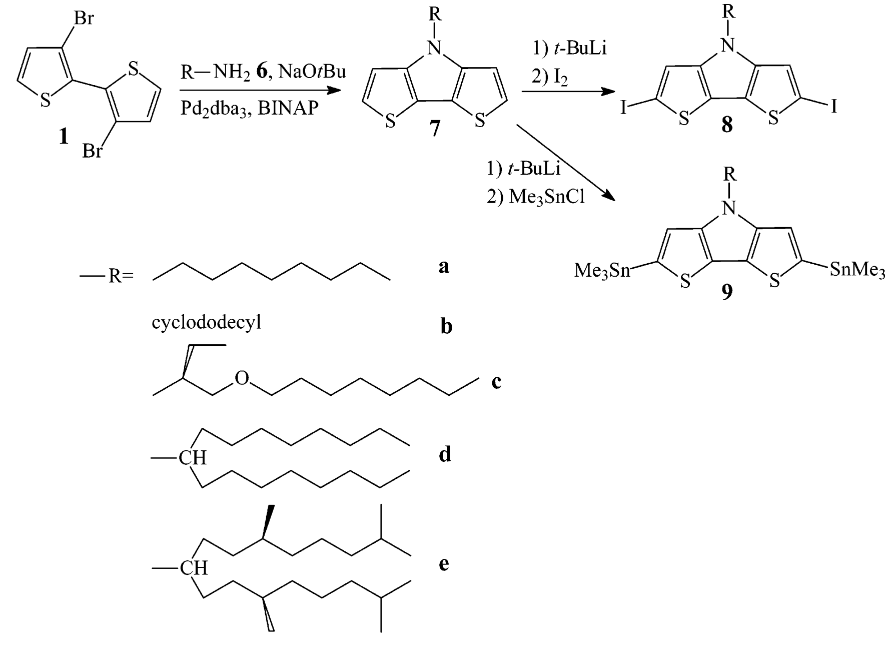
Stille-Type Polymerization (P*-Stil). A general procedure is as follows: A solution of distannylated monomer **9** (1.00 mmol), diiodated monomer **8** (1.00 mmol), Pd_2dba_3 (22.9 mg, 0.0250 mmol), and $AsPh_3$ (61.2 mg, 0.200 mmol) in dry THF (30 mL) was purged with argon for 0.5 h and then gently refluxed for 75 h. After cooling, the polymer was concentrated and poured into methanol. The precipitate was filtered off, and the polymer was further purified by Soxhlet extractions using successively acetone, hexanes, and chloroform. The chloroform-soluble fraction (or hexanes-soluble fraction in the case of **Pe-Stil**) was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

Results and Discussion

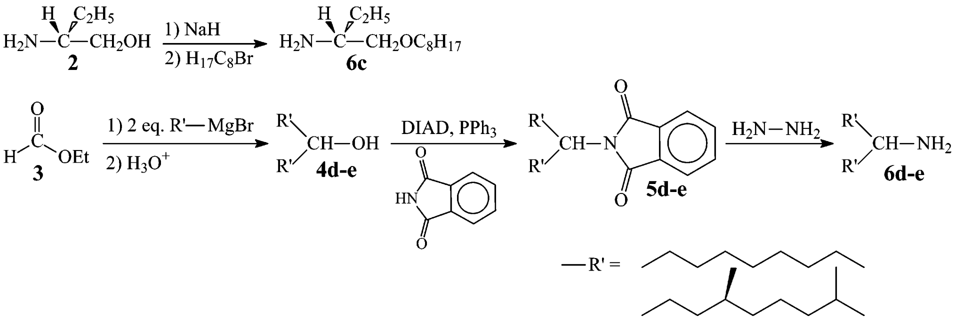
The structure of the polymers is presented in Figure 1. All polymers are substituted on the N atom with progressively bulkier groups. Both achiral and chiral side chains are employed. **Pa-ox** has already been prepared—albeit under different conditions—and was only incorporated for comparison.[2,3] Apart from variation in the molecular structure, the polymers were prepared using three different methodologies: an oxidative polymerization, a Stille-coupling reaction, and a Yamamoto-type polymerization.[8] The code of the polymers (**Pa,b,c,d,e-ox,Stil,Yam**) refers to the nature of the side-chain (**a**−**e**) and the polymerization method employed (**ox**idatively**, Stil**le, and **Yam**amoto).

Monomer Synthesis. The dithienopyrrole building blocks were synthesized according to our previously reported method, starting from 3,3′-dibromo-2,2′-bithiophene (**1**) and the ap-

Scheme 1. Monomer Synthesis



Scheme 2. Synthesis of the Amines 6c−e



propriate amines **6** (Scheme 1).[7] Except for **7b**, all dithienopyrroles could easily be prepared in high yields.

While amines **6a,b** were commercially available, **6c** was prepared from **2**, which was deprotonated with NaH and then reacted with octyl bromide. The formation of the alkoxide and the use of only 1 equiv of bromide were essential to prevent substantial *N*-alkylation. The amines **6d,e** were prepared starting from ethyl formate **3**, which was converted to the secundary alcohol by reaction with 2 equiv of Grignard reagent. Next, using a Mitsunobu reaction, the *N*-substituted phthalimides were prepared, which were finally converted to the corresponding amines by hydrazinolysis (Scheme 2).

In order to perform Stille-coupling reactions, diiodo- and di(trimethyltin)-substituted dithienopyrroles were prepared. This was accomplished by reacting the dithienopyrroles **7d,e** with 2.1 equiv of *t*-BuLi in diethyl ether at room temperature. The reaction can be driven to completeness by working at sufficiently low dilution. Next, I_2 or trimethyltin choride was added. Since distannylated dithienopyrroles degrade during purification by column chromatography,[9] a complete formation of the dilithium salt was necessary for the preparation of **9d,e** which was sufficiently pure for polymerization after reaction.

Polymer Synthesis. The polymers were prepared by three different methodologies (Scheme 3). First, oxidative polymerizations were employed. Different oxidants,[10] i.e., $FeCl_3$, $MoCl_5$, $TiCl_4$, and $RuCl_3$, were used to polymerize **7a**. In terms of molecular weight, yields, and especially regioregularity ($\alpha-\alpha$ vs $\alpha-\beta$ couplings, as determined by ^1H NMR spectroscopy) of the resulting polymers, $RuCl_3$ was superior to other oxidants. Therefore, all other dithienopyrroles were oxidatively polymerized with $RuCl_3$. Next, two nonoxidative methodologies for the preparation of PDTPs were employed, i.e., a Stille-coupling reaction and a Yamamoto-type polymerization. We must note that—to the best of our knowledge—PDTPs have never been

Scheme 3. Synthesis of the Polymers: (a) Oxidative Polymerization; (b) Using Stille-Couplings; (c) Yamamoto-Type Polymerization

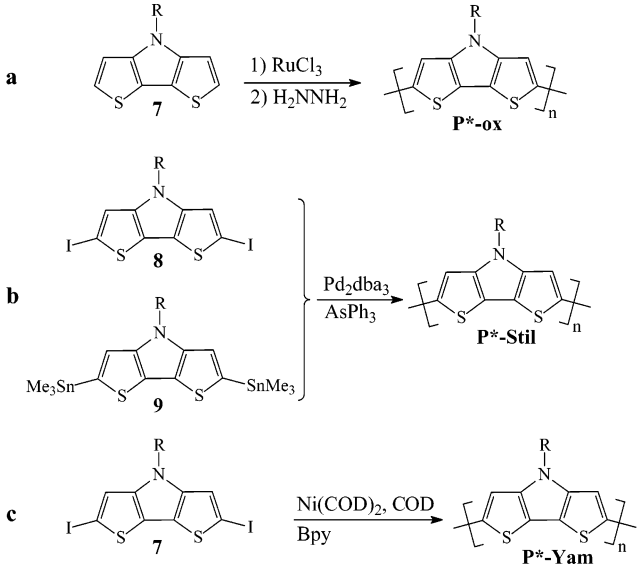


Table 1. Yields, Molecular Weights, Polydispersity, and Electrochemical Data of the Polymers

polymer	yield[a]/%	$\bar{M}_n$[b]/kg mol^{-1} (DP)[c]	D[b]	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V
Pa-ox	23	2.0 (7)	1.3	0.63	0.48	0.55
Pb-ox	14	2.9 (8)	10	0.67	0.48	0.57
Pc-ox	22	15 (41)	4.2	0.52	0.40	0.46
Pd-ox	25	50 (120)	12	0.60	0.43	0.51
Pd-Stil	62	280 (673)	4.5	0.64	0.44	0.54
Pd-Yam	9	80 (192)	6.2	0.64	0.44	0.54
Pe-ox	13	25 (53)	13	0.62	0.44	0.53
Pe-Stil	51[d]	120 (254)	3.5	0.60	0.45	0.52
Pe-Yam	2	19 (40)	10	0.70	0.48	0.59

[a] Of the chloroform-soluble fraction. [b] Determined by GPC in THF toward polystyrene standards. [c] Degree of polymerization. [d] Of the hexanes-soluble fraction.

prepared in a nonoxidative way, although, as will be shown, these methodologies are promising approaches for the preparation of these materials. The polymerization conditions for the Stille-couplings (Pd_2dba_3, $AsPh_3$) were chosen to obtain optimal molecular weights and yields.[11] The Yamamoto-type polymerization was carried out on the diiodo-functionalized compounds using $Ni(COD)_2$ as reagent in the presence of 1,5-cyclooctadiene (COD) and 2,2′-bipyridine (Bpy).[8]

After polymerization, the oxidatively prepared polymers were isolated in their oxidized state and were reduced by refluxing the polymers in a THF/hydrazine mixture for 2 h. All polymers were washed with acetone and hexanes using a Soxhlet apparatus to remove byproducts and oligomers. Finally, the polymers were extracted with chloroform, precipitated into methanol, and dried. **Pe-Stil,** however, dissolved completely in hexanes and was not extracted with chloroform. In the case of oxidatively and Yamamoto-polymerized polymers, a significant fraction of insoluble material was isolated, while the Stille-polymerized polymers **Pd-Stil** and **Pe-Stil** were completely soluble in hexanes and/or chloroform.

Yields, Solubility, and GPC Analysis. The yields of all polymers are presented in Table 1. They essentially depend on the polymerization methodology: oxidative polymerization leads to ∼15−25% yields, while Stille-couplings result in much higher polymer yields (∼50−60% after purification); Yamamoto-type polymerizations lead to very low yields. The yields are very dependent on the amount of insoluble material. Oxidatively and Yamamoto-polymerized materials show a large insoluble fraction, while Stille-coupled polymers are completely soluble. Moreover, as will be shown, GPC analysis reveals that the choroform-soluble fraction of polymers prepared by a Stille reaction is significantly *higher* in molecular weight than the chloroform-soluble fraction of polymers prepared by oxidative or Yamamoto-type polymerization. The presence of a (large) insoluble fraction in these methodologies can therefore not only be due to a reduced solubility caused by a too large molecular weight. Instead, it is more likely that, for instance in the case of the oxidative polymerization, the insolubility is caused by cross-linking. A possible pathway of cross-linking in oxidative polymerization could be the formation of $\alpha-\beta$ and $\beta-\beta$ couplings.

While the polymerization methods seem to be the major factor controlling the yields, the solubility of the different polymers is governed by the side chain. The solubility of **Pa-ox** is ∼10 g/L in chloroform, while it rises to ∼100 g/L for **Pd-ox** (and even more for **Pe-ox**). It is clear that the increased solubility of **Pd-ox** must be due to the reduction of the π-stacking, caused by the bulkier side chains.

The molecular weights of the polymers were determined by GPC in THF toward polystyrene standards. From Table 1, it is clear that it is possible to prepare soluble PDTPs with high molecular weights. Since GPC is not an absolute technique for the determination of molecular weights and the hydrodynamic volumes of the standard (polystyrene) and the polymers studied can expected to be drastically different, the absolute value of the molecular weights must be put into perspective. On the other hand, since all polymers studied have an analogous structure, GPC remains an excellent method to compare their molecular weights. The molecular weight of the (soluble) fraction seems to be dependent on both the bulkiness of the side chain and the polymerization method. On one hand, bulky side chains make a strong π-stacking impossible, which increases the solubility and prevents precipitation of the polymer during its synthesis. On the other hand, if **Pd,e-ox**, **Pd,e-Stil**, and **Pd,e-Yam,** which only differ in their polymerization methodology, are compared, it is clear that polymers prepared by Stille-couplings show the highest molecular weights and lowest polydispersities. Yamamoto-polymerized PDTPs show a very broad, multimodal weight distribution, which explains the high polydispersities.

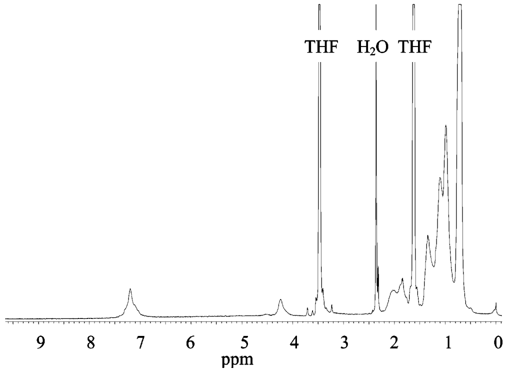


Figure 2. ^1H NMR spectrum of **Pe-Stil** in THF-d_8.

NMR and DSC. The molecular structure of the polymers is confirmed by ^1H NMR spectroscopy. The ^1H NMR spectrum of **Pe-Stil** is displayed in Figure 2. As can been seen, no defects are present, which confirms the regular structure, without defects. Moreover, the absence of end groups points at high molecular weights, which is in agreement with the GPC data.

DSC analysis reveals that all polymers do not degrade below 270 °C nor melt. **Pc-ox**, however, show a glass transition near 174 °C (heating, second cycle, scanning rate = 20 °C/min).

Cyclic Voltammetry. The potential of the peak anodic current (E_{pa}) and peak cathodic current (E_{pc}) of films, deposited from chloroform solution, were measured using cyclic voltammetry. In order to obtain films of equal thickness, the concentration of the solution and film forming conditions were kept constant. $E_{1/2}$ is roughly independent (0.51−0.59 V) of the side chain in the polymers (except for **Pc-ox**; the reason for the lower $E_{1/2}$ in these materials is unclear). Moreover, $E_{1/2}$ was independent of the scanning rate, and the oxidation and back-reduction could be repeated several times without significant change in the voltammogram. On the other hand, the *shape* of the oxidation wave appears to be dependent on the nature of the side chain: While PDTPs substituted with linear and slighly branched side chains are reported to give broad oxidation waves[3] (see also Figure 3), the redox wave of **Pc−e** is much more defined (Figure 3 and Supporting Information). The oxidation of these polymers is pseudo-reversible.

The reason for the differences in shape can be explained in terms of the molecular weights. **Pa-ox** and **Pb-ox** are low molecular weight materials (DP = 7−8), whose possible effective conjugation lengths are longer than the actual length of the polymers. Consequently, the sample appears as a mixture

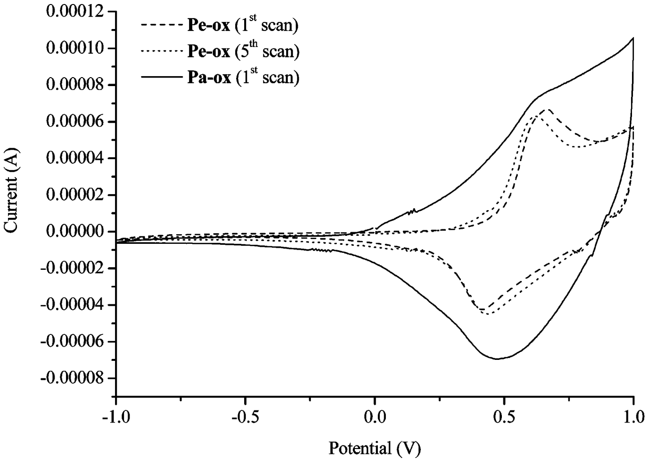


Figure 3. Cyclic voltammograms of **Pa-ox** (first scan) and **Pe-ox** (first and fifth scan) in acetonitrile (0.1 M Bu_4NBF_4). Scanning rate = 50 mV/s.

Table 2. λ_{max} of the Polymers in Solution and Film in Neutral and Oxidized State

	λ_{max} in solution[a]/nm		λ_{max} in film/nm		
polymer	neutral	oxidized[b]	neutral	oxidized[c]	band gap/eV[d]
Pa-ox	522	714, 1411	526	764, 1676	1.8
Pb-ox	493	823, 1740	506	755, 1347	2.0
Pc-ox	551	876, >2000	562	761, >2000	1.9
Pd-ox	545	875, >2000	556	746, >2000	1.9
Pd-Stil	544	875, >2000	541	767, >2000	1.9
Pd-Yam	539	867, >2000	550	785, >2000	1.9
Pe-ox	551	875, >2000	555	762, >2000	1.9
Pe-Stil	549	875, >2000	547	761, >2000	1.9
Pe-Yam	505	862, >2000	516	801, >2000	1.9

[a] In THF solution. [b] By addition of a concentrated I_2 solution (in THF, 400 mol % I_2). [c] By exposure to I_2 vapor. [d] In film.

of sites with different conjugation lengths and, consequently, electroactive properties, giving rise to a broad oxidation wave. The broadness of the wave can also be explained by further polymerization of the oligomers during the measurements, but in that case, the voltammogram should be altered.[1a] On the other hand, the effective conjugation length of the high molecular weight polymers (**Pc-e**) is not governed by the molecular weight, resulting in equally electroactive sites and, as a consequence, more defined redox waves. These findings are consistent with the UV−vis data (see below).

The low $E_{1/2}$ of the polymers ensures a smooth oxidation of the polymers. As already has been shown,[2] PDTPs can easily be oxidized in both film and solution using, for instance, I_2 as an oxidant. Finally, the onset of the oxidation wave was ~0.45 V in **Pb-e**. From this value, the HOMO level of the polymers can be calculated at −4.64 eV.

UV−vis and CD Spectroscopy. λ_{max} and the optical band gaps are displayed in Table 2. Although the substituent—and, consequently, the potential steric hindrance—is smallest in **Pa-ox**, λ_{max} is the lower in these polymers than in **Pc-e**. **Pa-ox** shows a low molecular weight which corresponds to only ~7 repeating units (Table 1). Ogawa et al. have shown that the possible conjugation length of low molecular weight, *N*-substituted PDTPs is higher than the number of repeating units present in **Pa-ox** and that λ_{max} therefore depends on its molecular weight.[3] On the other hand, **Pc-ox**, **Pd**, and **Pe** (except for **Pe-Yam**), which are all substituted with substituents of different bulkiness, show approximately the same λ_{max}, regardless of the number of repeating units. Moreover, compared with **Pa,b**, λ_{max} is clearly red-shifted and a vibronic fine-structure appears (Figure 4). In these polymers, the number of repeating units is higher than in **Pa,b** (>40)—also significantly higher than the conjugation length of the polymers. The relative independence of λ_{max} with respect to the size of the substituent also indicates that—even if bulky groups are employed—the conjugation between two DTP moieties is not disrupted by the bulky side chains. These observations, together with the CV data, suggest that *N*-substituted PDTPs appear in film as rigid, highly conjugated polymers.

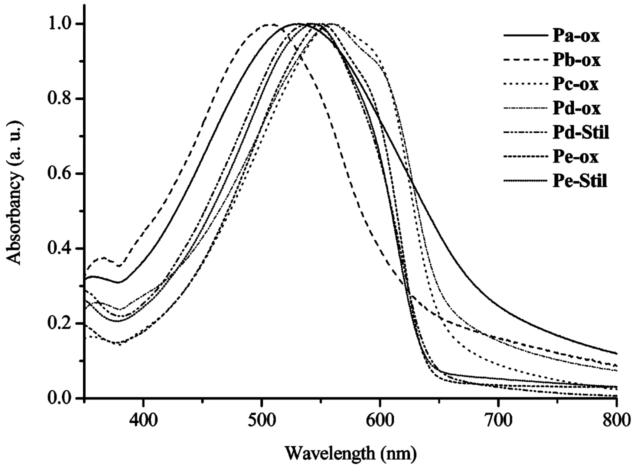


Figure 4. UV−vis spectra of films of **Pa-ox**, **Pb-ox**, **Pc-ox**, **Pd-ox**, **Pd-Stil**, **Pe-ox**, and **Pe-Stil**. The spectra are normalized to account for differences in thickness.

The band gap was calculated from the onset of the absorption band. The relative independence of the band gaps of the polymers can be explained by the very steep cutoff of the higher molecular weight polymers: in those polymers, the increase in λ_{max} is compensated by the steeper cutoff. On the other hand, the steep cutoff again confirms the fact the polymer consists of chromophores of equal conjugation length, pointing at very regular structure and high molecular weights (significantly higher than the conjugation lengths).

In solution, the same supramolecular structure can be deduced from the high λ_{max} of the polymers in solution and the fact that only a very small red-shift is observed upon transition from solution to film. Indeed, if λ_{max} of the PDTPs is compared with λ_{max} of regioregular poly(3-alkylthiophene)s (~440 and ~520 nm in solution and film, respectively[12]), the high λ_{max} of the PDTPs in solution and the small red-shift are conspicuous. Regioregular poly(3-alkylthiophene)s adopt a poorly conjugated random-coil-like structure in good solvents but planarize and aggregate upon addition of nonsolvents or in film.[12] That planarization and stacking are accompanied by a large red-shift and the appearance of a clear vibronic fine-structure. The small red-shift and the high λ_{max} of PDTPs in solution make us believe that the polymers already appear as highly conjugated, rigid rods in solution, which only slightly more planarize and stack upon transition to a film (since they are already planar), which is in accordance with previous hypotheses.[2,3] Stacking, if present, can also slightly extend the conjugation length.

Because of the use of the electron-rich DTP moieties, PDTPs can easily be oxidized, and they remain oxidized from long periods of time.[2] Remarkably, the oxidized polymers show a higher λ_{max} in solution than in film (except for **Pa-ox**). This can be explained by the restricted mobility in the polymer chain in film. Indeed, oxidation is accompanied by planarization (to stabilize the positive charge) and that planarization is restricted in film (since this would require movements of the polymer chains in the film), while it is still possible in solution.

Although it is clear that the polymers appear as rigid rods in solution, which aggregate upon transition to film, the question still remains how effective and regular the supramolecular aggregation is. Circular dichroism has proven to be a very powerful tool in the determination of the supramolecular behavior of conjugated polymers and oligomers, provided of course that chiral side chains are present to distinguish between the two enantiomeric structures.[13] In general, three "types" of chiral structures can be distinguished: (i) chiral supramolecular stacking of linear, rigid systems, as, for instance, in regioregular poly(3-alkylthiophene)s,[6,14] (ii) a one-handed helical structure, as is the case in some substituted cis−transoid poly(acetylene)s,[15] and finally (iii) a twisted, ribbonlike structure, as found in 9,9-disubstituted poly(fluorene)s.[16] The benefit of CD spectroscopy is that, provided that the observed Cotton effects are due to supramolecular chirality (which is the case, vide infra), the presence of Cotton effects is direct proof of (chiral) stacking. Moreover, the "amount" of chirality, and therefore the effectiveness of the chiral stacking, can be expressed by the g_{abs} value, which is defined as $\Delta\epsilon/\epsilon$.

Pc-ox, **Pe-ox**, and **Pe-Stil** show only (very) small bisignate Cotton effects, indicating that the polymer chains are hardly chirally stacked, although in all cases, chiral side chains are used. Moreover, if **Pe-ox** ($g_{\mathrm{abs}} = 2 \times 10^{-4}$) and **Pe-Stil** ($g_{\mathrm{abs}} < 10^{-5}$), which differ only in their molecular weights, are compared, a clear difference in CD intensity is observed: the higher molecular weight polymer shows the smallest CD intensities. This can be explained by the less efficient and/or regular stacking of large, rigid macromolecules in comparison with smaller ones. This hypothesis is also confirmed by the more defined vibronic fine-structure presented in **Pd,e-ox** compared with **Pd,e-Stil. Pe-Yam**, which shows very high polydispersities, shows no Cotton effects. If we take the very low yields, high polydispersities, and poor (chir)optical properties of the polymers into account, it can be concluded that Yamamoto-type polymerization is not the most appropriate polymerization methodology for DTPs. The polymers were therefore not used in further experiments.

The aggregation behavior can also be observed in mixtures of a solvent (chloroform) and a nonsolvent (methanol), as has been shown for other polythiophenes:[6,14] upon addition of a nonsolvent, the polymers chains aggregate (Figure 5).

If the g_{abs} value in solution (3×10^{-4} for **Pe-ox** and 10^{-4} for **Pe-Stil**) are compared with those in film (2×10^{-4} for **Pe-ox** and $<10^{-5}$ for **Pe-Stil**), the g_{abs} value in solution is higher than in film, which can be explained by the higher flexibility in solution, which allows the formation of more "perfect" aggregates. It is also clear that increasing the molecular weight of the polymers decreases the g_{abs} value, which again confirms the less efficient chiral stacking of larger, rigid macromolecules than shorter ones. For comparison, typical g_{abs} values for films of regioregular poly(3-alkylthiophene)s[17a,b] and poly(3-alkoxythiophene)s[17c] are on the order of 10^{-3}−10^{-2}, which again points at a less "efficient" chiral packing of the PDTPs.

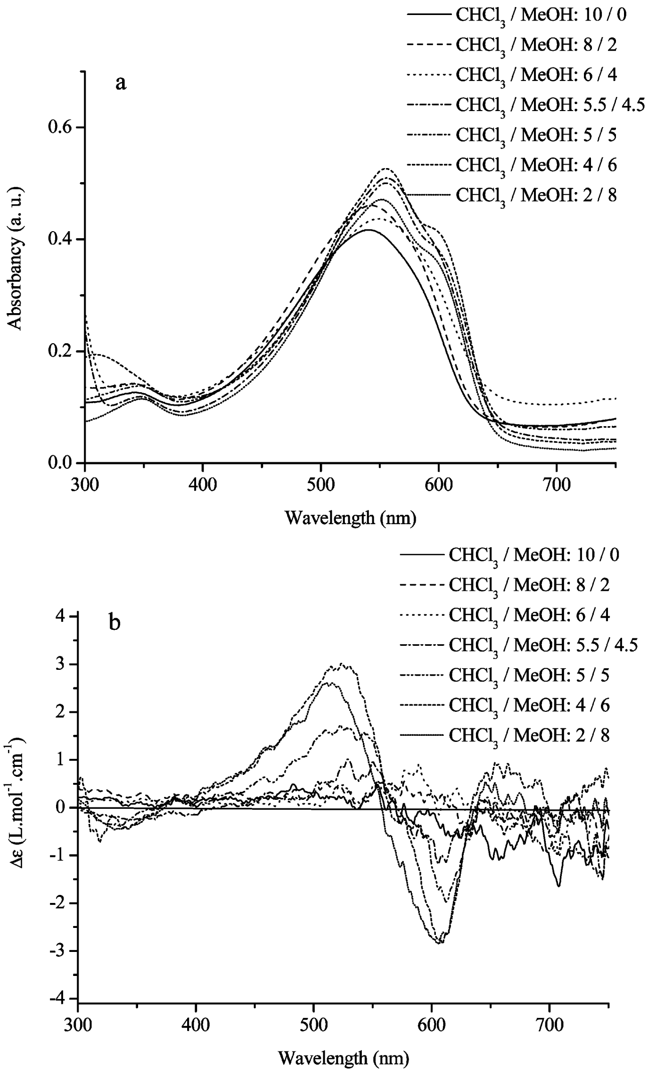


Figure 5. (a) UV−vis and (b) CD spectra of chloroform/methanol mixtures of **Pe-ox** ($c = 15$ mg/L).

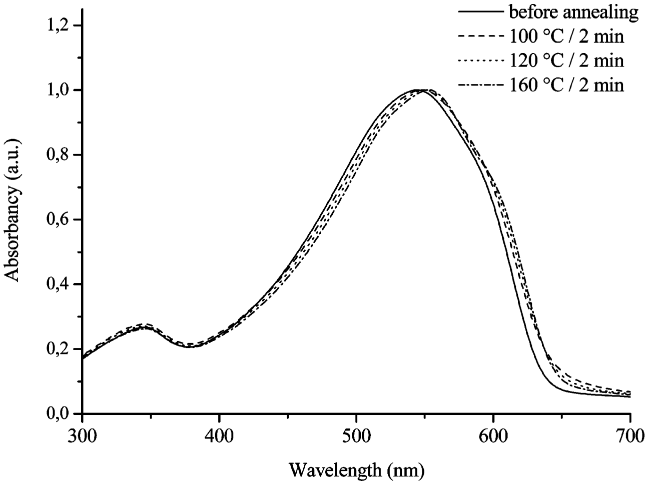


Figure 6. UV−vis spectra of the annealing of a spin-coated film (chloroform) of **Pe-Stil**. The film was first heated for 2 min at 100 °C, then for 2 min at 120 °C, and finally for 2 min at 160 °C.

Annealing of a film, spun from chloroform solution, at different temperatures for 2 min, leads to a small increase in $\lambda_{\max}$, together with the presence of a slightly more defined vibronic fine-structure (Figure 6). The observed change in UV−vis spectrum upon annealing is a common feature in conjugated oligomers and polymers and can be explained by the planarization of the conjugated chain and an evolution toward an altered, more efficient packing of the molecules. However, only a relatively small effect is present in the PDTPs, and again, the effect is stronger in the **Pe-ox** (lower molecular weight) than in **Pe-Stil**. This is consistent with the hypothesis of the polymers being rather stiff, rod-like macromolecules, with restricted molecular motions, and that higher molecular weights complicate the rearrangements. Quite surprisingly, when the annealed film is treated with choroform vapor, which is also often used to "anneal" the film, the original state is restored. Treatment of

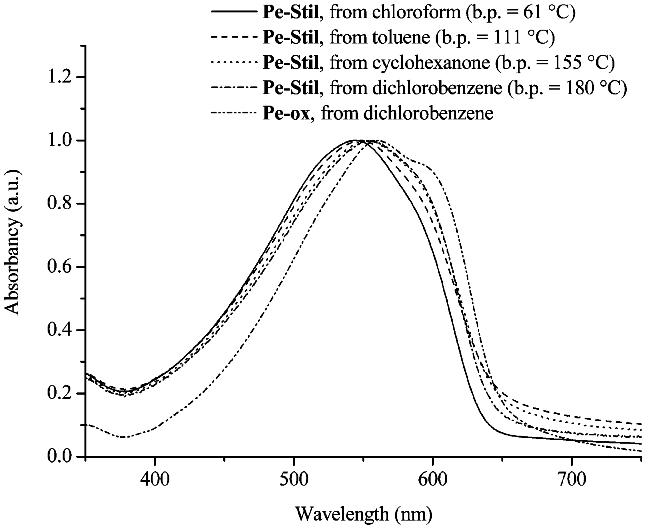


Figure 7. UV−vis spectrum of **Pe-Stil** spin-coated from different solvents.

an unannealled film with chloroform vapor does not change the spectrum.

When **Pe-Stil** was spin-coated from different solvents, a small red-shift, accompanied by a more defined vibronic fine-structure, was observed, if solvents with progressively higher boiling points are used (Figure 7). This confirms the above-mentioned trends. It has already been demonstrated for other conjugated polymers, for instance regioregular poly(3-hexylthiophene), that the boiling point of the solvent used and the speed of evaporation have an important effect of the properties of the resulting films.[18]

Finally, dilution experiments were carried out in order to distinguish between the possible forms of chirality (supramolecular stacking, helix, and twisted ribbon). A ratio of chloroform/methanol (1/1) was used since in that case the transition between the achiral and chiral state was intermediate (see Figure 5a,b). As follows from Figure 8, increasing the concentration leads to a hypsochromic shift together with an increase in vibronic fine-structure of the UV−vis spectra, while it also increases the CD effects. These observed concentration dependence clearly demonstrates that the observed Cotton effects are due to supramolecular stacking.

Fluorescence. The emission data of some selected polymers are summarized in Table 3. All spectra were recorded in THF. Cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol) (**Pa,c,d,e**) and rhodamin 6G (λ_{em} = 522 nm, Φ_f = 0.76 in water) (**Pb-ox**) were used as a reference, since its λ_{em} matches closely with those of the polymers. Since the rigidity of the backbone has a profound influence on the emission properties, fluorescence is an interesting tool to probe differences of the polymers. The fwhm$_{em}$ and the Stokes shift decrease with increasing rigidity, while the relatively high quantum yields of *N*-substituted PDTPs have also been ascribed to the rigidity of the polymer backbone.[3] It is clear that increasing the bulkiness of the side chain, which increases the molecular weight of the polymers, leads to smaller fwhm$_{em}$ and Stokes shift, while the quantum yield increases. The same trend are observed if Stille-coupling reactions are used instead of an oxidative polymerization (**Pe-ox**, lower molecular weight vs **Pe-Stil**, higher molecular weight): while the fwhm$_{em}$ and Stokes shift remain more or less the same, the quantum yield clearly increases. Consequently, the emission data support our hypothesis concerning the rigidity of the polymers (in solution) and concerning the influence of the molecular weight on the rigidity. Surprisingly, **Pb-ox** shows two emission peaks and large quantum yields.

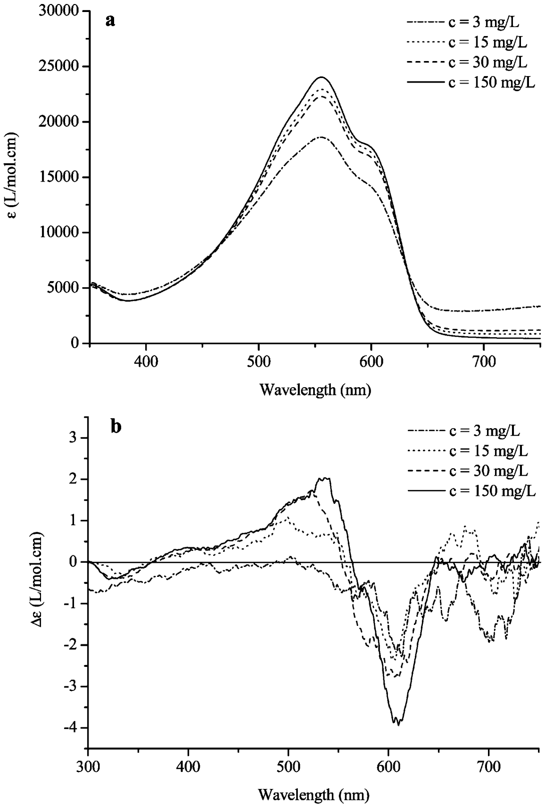


Figure 8. Concentration dependence in a chloroform/methanol (1/1) mixture of the (a) UV−vis and (b) CD spectrum of **Pe-ox**.

Table 3. Emission Data of the Polymers in THF Solution

polymer	λ_{ex}/nm	λ_{em}/nm	fwhm$_{em}$/cm^{-1}	Stokes shift/cm^{-1}	Φ_f[a]
Pa-ox	525	602	1792	2437	0.18[b]
Pb-ox	488	561	*c*	*c*	0.36[d]
Pc-ox	550	614	1144	1895	0.20
Pd-Stil	543	617	1196	2209	0.25
Pe-ox	550	617	1127	1975	0.28
Pe-Stil	549	618	1178	2034	0.32

[a] Measured toward cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol). [b] The quantum yield of higher molecular weight poly(*N*-octyldithienopyrrole) (obtained by intensive Soxhlet extractions), measured toward 9,10-diphenylanthracene (λ_{em} = 409 and 430 nm, Φ_f = 0.90), was reported to be 0.27.[3] The difference between the measured and already reported values can be explained by the use of another standard (cresyl violet perchlorate) and/or the difference in molecular weight. [c] A bimodal emission spectrum was obtained. [d] Measured toward rhodamin 6G (λ_{em} = 552 nm, Φ_f = 0.76 in water).

Conclusion

In conclusion, we have prepared poly(dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s in three different ways, i.e., an oxidative polymerization using RuCl$_3$, by Stille-couplings, and by a Yamamoto-type polymerization. In terms of yields, molecular weights, and optical properties, Stille-coupling reactions appeared to be the best polymerization method. We have shown that soluble poly(*N*-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s with large molecular weights can be prepared in high yields. The solubility of the polymers essentially depends on the nature (bulkiness) of the side chain, since bulky side chains weaken the π-stacking. The yields, and to a lesser extent the molecular weights, depend on the nature of the polymerization method. The polymers adopt a highly conjugated, rigid-rod-like structure in solution, which aggregate upon transition to film or in nonsolvents. The small red-shift and g_{abs} values indicate a poor (chiral) stacking. Moreover, stacking is more complicated in the higher molecular weight polymers. On the other hand, reaching a sufficient high molecular weight leads to well-defined oxidation waves (CV) and increased λ_{max}, together with the presence of the clear vibronic fine-structure and strong emission. Given the possibility to obtain high molecular weights, solubility, and yields, these polymers continue to be interesting, highly conjugated polymers.

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Supporting Information Available: Comparison of poly(*N*-octyldithienopyrrole) prepared using different oxidants, CV 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

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