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Identification and Quantification of Defect Structures in Poly(2,5-thienylene vinylene) Derivatives Prepared via the Dithiocarbamate Precursor Route by Means of NMR Spectroscopy on ^{13}C-Labeled Polymers

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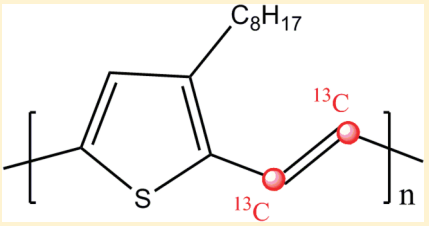
ABSTRACT: During the past decades several synthetic routes toward the low band gap polymer poly(2,5-thienylene vinylene) (PTV) and derivatives have been studied. This study describes an extensive NMR characterization of ^{13}C-labeled 3-octyl-PTV and its precursor polymer prepared via the dithiocarbamate route which is, since stable monomers are available, a promising route toward PTV derivatives. By introducing ^{13}C-labeled vinylene carbons, we were able to characterize these polymers in a quantitative way, taking the end groups and structural polymerization defects, which disturb the conjugated system, into account. Several NMR techniques and the synthesis of model compounds were used to fully assign the proton and carbon chemical shifts. Moreover, the classically used thermal conversion of the precursor toward the conjugated polymer has been compared to a smoother, acid-induced elimination procedure.



INTRODUCTION

During the past two decades rapid strides have been made in the field of conjugated polymers. Their semiconductor properties allow their use in all kinds of electronic devices, such as organic field effect transistors,[1,2] biosensors,[3] light-emitting diodes,[4,5] and photovoltaic cells.[6−9] The main advantage of such organic semiconductors is that their structure and thus their electro-optical properties can be tuned virtually to any combination of specifications needed for a dedicated application. For example, in polymeric bulk heterojunction solar cells the mismatch between the absorption spectrum of the active layer and the solar emission spectrum can be decreased by focusing on the design and synthesis of different classes of low band gap materials.[10−16] In this context poly(2,5-thienylene vinylene) (PTV) derivatives have been considered as a promising class of low band gap polymer.[17−22] The most efficient synthetic routes toward PTVs make use of the polymerization behavior of quinodimethane systems. They can be obtained via a base induced elimination in a premonomer of type **1g** (Schemes 1 and 2). On formation of the quinodimethane system, a fast polymerization reaction yields high molecular weight precursor polymers which can be converted in situ or ex situ to the conjugated structure. Substantial research efforts have been devoted to the optimization of these synthetic pathways toward PTV derivatives, e.g. the Wessling,[23−25] xanthate,[26,27] sulfinyl,[28,29] and dithiocarbamate[30,31] routes. The dithiocarbamate (DTC) route toward PTV, developed in our lab, has as main advantage that the premonomer is much more stable as compared to the premonomers of the other precursor routes and therefore allows the polymerization of better defined precursor polymers.

In this paper a thorough investigation is presented into the detection and identification of defect structures and end groups in 3-octyl-PTV (O-PTV) precursor polymers and their converted, still soluble, conjugated O-PTV polymers. Hereto, ^{13}C-labeled polymers were prepared by introducing ^{13}C labels in the premonomers. Quantitative NMR techniques and model compounds allowed for the identification of said defects. Moreover, the precursor polymer was converted to the conjugated polymer by a thermal as well as acid-induced conversion process. Comparison of the results obtained indicates that the acid-induced conversion proceeds smoother than the thermal-induced one.

EXPERIMENTAL SECTION

Materials. All the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether used in the synthesis were dried by distillation from sodium/benzophenone.

Analytical. ^{1}H and ^{13}C NMR spectra were taken on a Varian Inova 300 or 400 spectrometer from solutions in deuterated chloroform (D, 99.8%). The chemical shifts were calibrated by means of the (remaining) proton and carbon resonance signals of $CDCl_3$ (7.24 and 77.7 ppm for ^{1}H and ^{13}C, respectively). The T_{1C} relaxation decay times were determined via the inversion−recovery method. To quantify the

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amount of structural defects and end groups from the ^{13}C NMR spectra, the summed integration of three signals of the side chain (carbon atoms 17, 18, and 19) was taken as an internal reference to which the other resonances were normalized. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Laboratories) by size exclusion chromatography (SEC). Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10 μm, 0.75 × 30 cm, Polymer Laboratories) and a relative index (RI) detector (Shodex). GC/MS analyses were carried out on a TSQ-70 and Voyager mass spectrometer (Thermoquest); capillary column: Chrompack Cpsil5CB or Cpsil8CB.

Fourier transform-infrared spectroscopy (FT-IR) was performed on a Perkin-Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans).

Ultraviolet−visible spectroscopy (UV−vis) was performed on a Varian cary 500 UV−vis−NIR spectrophotometer (interval: 1 nm; scan rate: 600 nm/min, continuous run from 200 to 700 nm).

TLC analyses were made on Merck aluminum sheets, 20 × 20 cm, covered with silica gel 60 F_{254}.

Synthesis and Characterization. *A. Synthesis of the ^{13}C-Labeled Monomer (**1g**).* The synthesis of 3-octylthiophene **1b** and 3-octyl-2,5-dibromothiophene **1c** has been described elsewhere.[32]

*Synthesis of 3-Octyl-2,5-thiophenedicarboxaldehyde (**1d**).* In a three-necked round-bottom flask a solution of 2,5-dibromo-3-octylthiophene, **1c** (4.3 g, 12 mmol), in THF (100 mL) was stirred under a nitrogen atmosphere at −78 °C. A solution of *n*-butyllithium (16.7 mL, 27 mmol of a 1.6 M solution in hexane) was slowly added with a cannula, the mixture was stirred for 30 min, and afterward ^{13}C enriched DMF (2.0 g, 0.27 mol), previously distilled, was slowly added. The resulting mixture was stirred for 12 h at room temperature. HCl (2 M, 50 mL) was added to quench the excess of *n*-BuLi followed by extraction with chloroform. The organic layers were dried over $MgSO_4$, and the obtained compound was purified by column chromatography on silica gel with chloroform/hexane (1/1) as a solvent. The dialdehyde **1d** was obtained as orange oil (1.8 g, yield 58%). ^1H NMR ($CDCl_3$, δ in ppm, J in Hz): 10.12 (d, $^1J_{H-13C}$ = 180, 1H), 9.95 (d, $^1J_{H-13C}$ = 180, 1H), 7.63 (d, J = 3.5, 1H), 2.97 (t, J = 8.1, 2H), 1.73−1.62 (m, 2H), 1.41−1.20 (m, 10H), 0.86 (t, J = 7.3, 3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 184.1, 183.7, 152.7, 148.9, 144.3, 138.2, 32.5, 31.9, 30.0, 29.9, 29.8, 29.2, 23.3, 14.8. MS (EI, m/e): 254 (M^+).

*Synthesis of 3-Octyl-2,5-bis(hydroxymethyl)thiophene (**1e**).* In a three-necked round-bottom flask a mixture of $LiAlH_4$ (0.54 g, 14 mmol) in dry THF (50 mL) was made under an argon atmosphere. This slurry was cooled to 0 °C, and the dialdehyde **1d** (1.8 g, 7.1 mmol) in THF (50 mL) was slowly added with a dropping funnel. When the addition was completed, the slurry was heated at reflux temperature for 5 h. Afterward, the mixture was placed in an ice bath and quenched very careful with water and an aqueous 15% NaOH solution. The solution was extracted with diethyl ether and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The diol **1e** was obtained as a yellow oil in a yield of 96% (1.7 g). ^1H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.76 (d, $^3J_{H-13C}$ = 3.2, 1H), 4.73 (d, J = 144, 2H), 4.70 (d, J = 144, 2H), 2.52 (t, J = 8.0, 2H), 1.57−1.48 (m, 2H), 1.34−1.19 (m, 10H), 0.85 (t, J = 6.4, 3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 142.6, 140.9, 137.8, 128.3, 60.9, 58.4, 32.5, 32.3, 31.7, 30.1, 29.9, 28.9, 23.3, 14.8. MS (EI, m/e): 224 (M^+ − hydroxyl functions, M^+ is not stable).

*Synthesis of 3-Octyl-2,5-bis(chloromethyl)thiophene (**1f**).* To a cooled (0 °C), stirred solution of diol **1e** (1.7 g, 6.8 mmol) in THF (30 mL) was slowly added a solution of $SOCl_2$ (2.16 g, 18 mmol) in THF (40 mL). The temperature of the reaction mixture was allowed to increase to RT under continuous stirring for 1 h. Then, the mixture was cooled down again to 0 °C, and a saturated sodium carbonate solution was added dropwise until neutral. The mixture was extracted with diethyl ether and dried over $MgSO_4$. The solvent was evaporated, and the highly reactive dichloride **1f** was obtained as an orange oil. Because of the high reactivity of **1f**, the dichloride was used in the next reaction step without purification or characterization.

*Synthesis of 3-Octyl-2,5-diylbismethylene N,N-Diethyldithiocarbamate (**1g**).* To a solution of **1f** (2.08 g, 4.0 mmol) in ethanol (50 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.61 g, 16 mmol) was added as solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The monomer **1g** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (2.5 g, 67%). ^1H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.75 (d, J = 3.3, 1H), 4.65 (d, J = 146, 2H), 4.58 (d, J = 146, 2H), 4.01 (q, J = 6.8, 4H), 3.68 (q, J = 6.8, 4H), 2.48 (t, J = 8.0, 2H), 1.59−1.49 (m, 2H), 1.33−1.22 (m, 16H), 0.85 (t, J = 6.8, 3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 195.3, 195.0, 141.9, 137.8, 131.4, 129.6, 49.9, 47.3, 32.5, 31.2, 30.1, 29.8, 29.1, 23.3, 14.7, 13.1, 12.2. MS (CI, m/e): 517 (M^+).

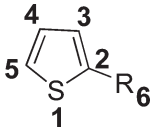
*B. Synthesis of the ^{13}C-Labeled Precursor Polymer **1h**.* The monomer **1g** (0.93 g, 1.8 mmol) was previously freeze-dried. A solution with a monomer concentration of 0.4 M in dry THF was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (3.6 mL of a 1.0 M solution in THF) was added in one go to the stirring monomer solution. The resulting mixture was stirred for 90 min under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water, and the water layer was neutralized with diluted HCl before extraction with chloroform. The solvent of the combined organic layers was evaporated under reduced pressure, and a second precipitation was performed in pure cold methanol. The polymer **1h** was collected and dried in vacuo (0.45 g, yield 67%). The polymer has been fractionated by multiple reversed precipitations (the polymer was solved in $CHCl_3$ and MeOH was added dropwise until the high molecular weight fraction precipitated) to collect the high molecular weight fraction (180 mg = precursor polymer **1D** (large batch)).

Polymers **1A** and **1B** are the low and high molecular weight fractions of a small polymerization batch. Starting from 280 mg (5.4×10^{-4} mol) of monomer **1g**, 0.13 g (yield 65%) of precursor polymer **1h** was obtained. After multiple reversed precipitations, 45 mg of high molecular weight and 54 mg of low molecular weight precursor polymer were obtained. Precursor polymer **1C** is the isolated high molecular weight fraction of another small batch. Here 210 mg of precursor polymer **1h** was obtained from 442 mg (8.5×10^{-4} mol) monomer **1g** (yield 67%). After multiple reversed precipitations, 61 mg of high molecular weight polymer was collected. IR (in cm^{-1}): 2931, 2846, 1486, 1415, 1268, 1206. SEC: $M_w = 4.6 \times 10^3$; PD = 6.2 (batch **1A**); $M_w = 6.8 \times 10^3$; PD = 5.0 (batch **1B**); $M_w = 8.3 \times 10^3$; PD = 3.5 (batch **1C**); $M_w = 18.8 \times 10^3$; PD = 3.4 (batch **1D**). ^1H NMR ($CDCl_3$, δ in ppm, J in Hz): 6.49 (1H), 5.35 (1H), 3.96 (2H), 3.66 (2H), 3.17 (2H), 2.28 (2H), 1.40−1.05 (18H), 0.85 (3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 194.7, 140.2, 139.3, 134.4, 128.4, 53.3, 49.8, 47.4, 37.2, 32.7, 31.6, 30.4, 30.1, 29.0, 23.4, 14.9, 13.4, 12.3.

*C. Synthesis of the ^{13}C-Labeled Polymer **1i**. Thermal Conversion.* The precursor polymer **1h** (batch **1D**: 60 mg, 0.16 mmol) was dissolved in *o*-dichlorobenzene (5 mL) and refluxed for 1 h. After being cooled, the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol, and dried in vacuo. A purple/black solid was obtained (25 mg, yield 70%). UV−vis: λ_{max} = 574 nm (shoulder: 611 nm). SEC: $M_w = 48 \times 10^3$; PD = 2.2. ^1H NMR ($CDCl_3$): see chemical shifts of **1h** except for the signals of the dithiocarbamate group which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 6.8−6.9 ppm. ^{13}C NMR ($CDCl_3$): see chemical shifts of **1h** except for the dithiocarbamate signals which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 121 ppm.

Acid-Induced Conversion. The precursor polymer **1h** (batch **1D**: 60 mg, 0.16 mmol) was dissolved in *o*-dichlorobenzene (5 mL) and heated until 70 °C before trifluoroacetic acid (0.018 mL, 0.24 mmol) was added. The solution was stirred for 10 min at 70 °C. After being cooled, the solution was poured into H_2O and extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the obtained slurry was precipitated in MeOH, filtered off, and dried in vacuo. A purple/black solid was obtained (34 mg, yield 97%). UV−vis: λ_{max} = 574 nm (shoulder: 614 nm). SEC: $M_w = 109 \times 10^3$; PD = 2.8. ^{1}H NMR ($CDCl_3$): see chemical shifts of **1h** except for the signals of the dithiocarbamate group which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 6.8−6.9 ppm. ^{13}C NMR ($CDCl_3$): see chemical shifts of **1h** except for the dithiocarbamate signals which disappear during elimination and the ^{13}C-labeled positions which form a double bond around 121 ppm.

D. Synthesis of Model Compounds for End Groups. The chemical shifts of the model compounds are assigned using the numbering system in the following figure:



Model compound **2a**: 2-thiophene-carbaldehyde (commercially available). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 9.91 (d, J = 1.2, 1H, **6**), 7.77 (dd, J_1 = 3.9, J_2 = 1.2, 1H, **5**), 7.75 (dt, J_1 = 4.9, J_2 = 1.2, 1H, **3**), 7.20 (dd, J_1 = 4.9, J_2 = 3.9, 1H, **4**). ^{13}C NMR ($CDCl_3$, δ in ppm): 183.7 (**6**), 144.6 (**2**), 137.0 (**3**), 135.8 (**5**), 129.0 (**4**).

Model compound **2b**: 2-thiophene methanol. A solution of **2a** (3 g, 27 mmol) in a 1:1 mixture of methanol and CH_2Cl_2 was cooled to 0 °C, and $NaBH_4$ (1.5 g, 40 mmol) was added as a solid. The mixture was stirred overnight and afterward quenched by the addition of H_2O (50 mL), followed by an extraction with Et_2O. The organic layers were dried over $MgSO_4$, and the obtained compound was purified by column chromatography on silica gel with hexane as a solvent. The alcohol **2b** was obtained as a colorless oil in a yield of 93% (2.9 g). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 7.27 (dd, J_1 = 5.0, J_2 = 1.3, 1H, **5**), 7.00 (m, 1H, **3**), 6.96 (dd, J_1 = 5.0, J_2 = 3.5, 1H, **4**), 4.82 (d, J = 3.5, 2H, **6**), 1.79 (s, 1H, **6′**). ^{13}C NMR ($CDCl_3$, δ in ppm): 144.2 (**2**), 127.0 (**3**), 125.6 (**4**), 125.5 (**5**), 59.3 (**6**).

Model compound **2c**: 2-thiophenecarboxylic acid (commercially available). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 12.50 (s, 1H, **6**), 7.89 (dd, J_1 = 3.8, J_2 = 1.2, 1H, **3**), 7.64 (dd, J_1 = 5.0, J_2 = 1.2, 1H, **5**), 7.13 (dd, J_1 = 5.0, J_2 = 3.8, 1H, **4**). ^{13}C NMR ($CDCl_3$, δ in ppm): 168.8 (**6**), 135.8 (**3**), 134.8 (**5**), 133.5 (**2**), 128.8 (**4**).

*E. Synthesis of Model Compounds for Structural Defects in the Precursor Polymer. Synthesis of 2-(Chloromethyl)thiophene (**2g**).* A solution of $SOCl_2$ (6.9 g, 58 mmol) in dry CH_2Cl_2 (40 mL) was made in a three-necked round-bottom flask. A solution of the alcohol **2b** (3 g, 26 mmol) in dry THF (20 mL) was added dropwise at 0 °C, and the reaction mixture has been stirred for 30 min at room temperature. The resulting reaction mixture was quenched with $NaHCO_3$ and extracted with CH_2Cl_2. The crude product was distilled by vacuum distillation to get a colorless oil (3.0 g, 23 mmol) in a good yield (88%). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 7.30 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 7.07 (dd, J_1 = 3.5, J_2 = 1.2, 1H), 6.94 (dd, J_1 = 5.1, J_2 = 3.5, 1H), 4.80 (s, 2H). ^{13}C NMR ($CDCl_3$, δ in ppm): 140.2, 127.8, 127.0 (2C), 40.5.

*Model Compound **2d**.* A three-necked round-bottom flask was filled with dry THF and sodium (0.9 g, 40 mmol). 2-(Chloromethyl)thiophene, **2g** (0.5 g, 3.8 mmol), was added dropwise to this dispersion. The reaction mixture was stirred overnight. Afterward, the reaction was quenched by the addition of ethanol (50 mL) and H_2O (50 mL). The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. The product **2d** was obtained as an oil (0.14 g, 0.7 mmol) after column chromatography (eluent: hexane) in a yield of 20%. ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 7.14 (dd, J_1 = 5.1, J_2 = 1.2, 2H), 6.93 (dd, J_1 = 5.1, J_2 = 3.6, 2H), 6.82 (dd, J_1 = 3.6, J_2 = 1.2, 2H), 3.21 (s, 4H). ^{13}C NMR ($CDCl_3$, δ in ppm): 144.3, 127.4, 125.3, 124.0, 32.8. MS (EI, *m*/*e*): 194 (M^+).

*Synthesis of **2j**.* A solution of thiophene, **2i** (10 g, 0.12 mol), and 2-thiophene acetyl chloride, **2h** (23.9 g, 0.15 mol), in toluene was stirred at room temperature. $AlCl_3$ (19.8 g, 0.15 mol) was added as a solid in a time frame of 10 min, and the reaction mixture was refluxed for 30 min. The solution was cooled to room temperature and quenched carefully with a 2 M HCl solution. The resulting reaction mixture was extracted with toluene, washed with HCl, NaOH, and H_2O, and dried over $MgSO_4$. The crude product was purified by distillation to give a colorless oil (6.6 g, 32 mmol, 29%). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 7.79 (dd, J_1 = 3.7, J_2 = 1.1, 1H), 7.65 (dd, J_1 = 5.0, J_2 = 1.1, 1H), 7.21 (dd, J_1 = 3.7, J_2 = 2.9, 1H), 7.13 (dd, J_1 = 3.8, J_2 = 5.0, 1H), 6.95−6.94 (m, 2H), 4.38 (s, 2H). ^{13}C NMR ($CDCl_3$, δ in ppm): 189.5, 143.8, 135.9, 135.1, 133.4, 128.9, 127.57, 127.55, 125.8, 40.8. MS (EI, *m*/*e*): 208 (M^+).

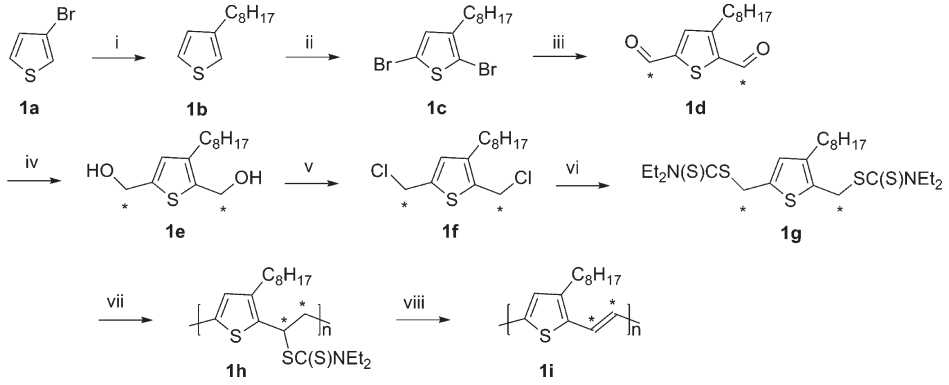
*Synthesis of **2k**.* A solution of **2j** (1 g, 4.8 mmol) was made in a mixture of CH_2Cl_2 and MeOH (1/1). The mixture was cooled to 0 °C, and $NaBH_4$ (0.36 g, 9.6 mmol) was added as a solid. The resulting solution was stirred for 12 h at room temperature. The reaction was quenched with NH_4Cl and extraction has been carried out by Et_2O and dried over $MgSO_4$. The crude product was purified by flash column chromatography to give a colorless oil (0.95 g, 4.5 mmol, 94%). ^{1}H NMR ($CDCl_3$, δ in ppm, *J* in Hz): 7.25 (dd, J_1 = 4.7, J_2 = 1.7, 1H), 7.17 (dd, J_1 = 5.1, J_2 = 1.2, 1H), 6.99−6.92 (m, 3H), 6.86 (dd, J_1 = 3.4, J_2 = 1.0, 1H), 5.14 (dd, J_1 = 6.9, J_2 = 5.6, 1H), 3.32 (dd, J_1 = 2.4, J_2 = 0.8, 2H). ^{13}C NMR ($CDCl_3$, δ in ppm): 147.6, 140.0, 127.4, 127.2, 127.1, 125.3, 125.1, 124.6, 71.4, 40.5. MS (EI, *m*/*e*): 209 (M^+).

*Synthesis of **2l**.* In a three-necked round-bottom flask, the alcohol **2k** (0.95 g, 4.5 mmol) was added dropwise to a stirred solution of $SOCl_2$ (1.18 g, 9.9 mmol) in THF (60 mL). The reaction mixture was stirred under a nitrogen atmosphere for 30 min. The solution was cooled to 0 °C and quenched carefully with a $NaHCO_3$ solution. The resulting reaction mixture was extracted with Et_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. Because of the unstable nature of the product **2l** (1.0 g, 4.4 mmol), the crude product has been used without further purification or characterization.

*Model Compound **2e**.* To a solution of the chloride **2l** (1.0 g, 4.4 mmol) in ethanol (25 mL), diethyldithiocarbamic acid sodium salt trihydrate (3.9 g, 18 mmol) was added as a solid. The mixture was stirred at ambient temperature overnight. Then, water was added and the desired monomer was extracted with diethyl ether and dried over $MgSO_4$. The model compound **2e** was obtained after column chromatography (eluent: chloroform/hexane 1/1) as a yellow oil (1.24 g, 3.6 mmol) in a yield of 59%. ^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.19 (dd, J_1 = 5.2, J_2 = 1.3, 1H), 7.06 (dd, J_1 = 5.0, J_2 = 1.3, 1H), 6.99 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 6.90 (dd, J_1 = 5.2, J_2 = 3.5, 1H), 6.84 (dd, J_1 = 5.0, J_2 = 3.5, 1H), 6.81 (dd, J_1 = 3.5, J_2 = 1.3, 1H), 5.62 (dd, J_1 = 9.9, J_2 = 4.7, 1H), 4.01 (q, J = 6.9, 2H), 3.84 (dd, J_1 = 14.8, J_2 = 4.7, 1H), 3.69 (q, J = 6.9, 2H), 3.43 (dd, J_1 = 14.8, J_2 = 9.9, 2H), 1.26 (t, J = 6.9, 3H), 1.25 (t, J = 6.9, 3H). ^{13}C NMR ($CDCl_3$, δ in ppm): 194.2, 143.1, 141.3, 127.4, 127.2, 127.1, 126.9, 125.7, 124.7, 52.9, 50.0, 47.4, 38.8, 13.2, 12.3.

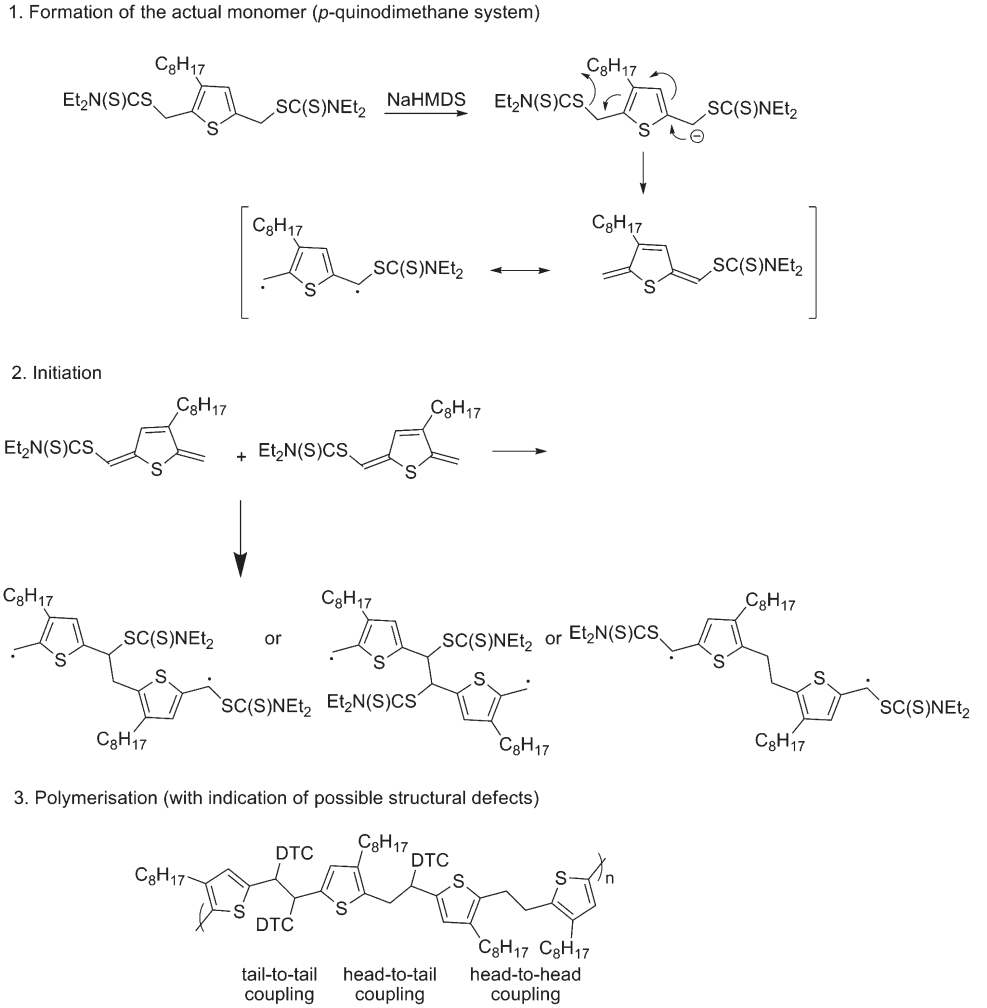
*F. Synthesis of Model Compounds for Structural Defects in the Conjugated Polymer. Synthesis of **2m**.* A suspension of Zn powder (6.9 g, 0.1 mol) was made in anhydrous THF (200 mL). This suspension was stirred at −10 °C under nitrogen atmosphere. $TiCl_4$ (10 g, 0.05 mol) was added dropwise to this suspension. The resulted mixture was heated at reflux temperature for 1 h. Afterward the mixture was cooled to room temperature, the aldehyde **2a** was added slowly and the reflux was continued for 4 h. The mixture was poured into a K_2CO_3 (10%) solution, extracted with Et_2O and the organic layers were dried over $MgSO_4$. The product was purified by means of column chromatography

Scheme 1. Synthetic Route toward ^{13}C-Labeled O-PTV[a]



[a] Reagents and conditions: (i) $BrMgC_8H_{17}$, $NiCl_2$(dppp); (ii) NBS, DMF; (iii) 1, BuLi; 2, ^{13}C-enriched DMF; (iv) $LiAlH_4$, THF; (v) $SOCl_2$, THF; (vi) $NaSC(S)NEt_2.3H_2O$, EtOH; (vii) NaHMDS, THF; (viii) ΔT or CF_3COOH.

Scheme 2. Polymerization Mechanism for the DTC Precursor Route



with petroleum ether as eluent. The product **2m** was obtained as a colorless powder (1.37 g, 13%). ^{1}H NMR ($CDCl_3$, δ in ppm, J in Hz): 7.18 (dd, J_1 = 5.0, J_2 = 1.1, 2H), 7.06 (s, 2H), 7.04 (dd, J_1 = 3.6, J_2 = 1.1, 2H), 6.99 (dd, J_1 = 5.0, J_2 = 3.6, 2H). ^{13}C NMR ($CDCl_3$, δ in ppm): 143.0, 128.3, 126.7, 125.0, 122.1. MS (EI, m/e): 192 (M^+).

RESULTS AND DISCUSSION

Synthesis of the ^{13}C-Labeled Monomer (1g). The first two steps in the synthesis of the ^{13}C-labeled monomer for octyl-PTV (O-PTV) are exactly the same as for the nonlabeled variant

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Table 1. Average Number of Repetition Units in the Precursor and Conjugated O-PTV Polymers As Calculated by GPC and NMR[a]

	GPC			NMR			
polymer	$M_n \times 10^3$ (g mol^{-1})	PD	av no. of repetition units	183.5 ppm	162.3 ppm	59.7 and 61.5 ppm	av no. of repetition units
precursor O-PTV							
1A	7.4	6.2	20	2.2%	9.3%	9.0%	10
1B	13.7	5.0	37	1.2%	4.4%	4.9%	19
1C	24	3.5	65	1.4%	2.0%	2.5%	34
1D	55	3.4	149	0.3%	1.1%	1.3%	74
O-PTV							
thermal	22	2.2	100	0.4%	1.0%	1.0%	83
acid	39	2.8	177	0.4%	0.7%	0.8%	105

[a] Molecular weight of the repetition units is 369 and 220 Da for the precursor and conjugated polymer, respectively. The conjugated O-PTVs were obtained by conversion of the precursor polymer **1D**.

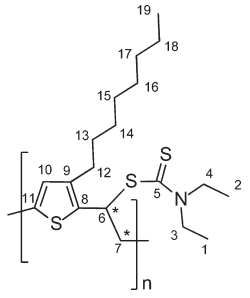


Figure 1. Chemical structure of precursor O-PTV including a carbon numbering scheme for the assignment of the resonances in the ^{13}C NMR spectra.

(Scheme 1).[32] First, the substitution of 3-bromothiophene (**1a**) by means of a Kumada coupling[33] has been performed, followed by bromination of the α-positions of the thiophene (**1b**).[34] In the third step of the reaction pathway, the ^{13}C label was incorporated. This was done by a metal−halogen exchange under the influence of *n*-BuLi, followed by addition of ^{13}C-enriched DMF, which results into the ^{13}C-labeled dialdehyde **1d**.[35] Thereafter, the dialdehyde **1d** was reduced with lithium aluminum hydride ($LiAlH_4$), followed by chlorination of the diol **1e** with thionyl choride ($SOCl_2$).[36] Because of the instability of the product **1f**, it must be converted in situ toward the bis(dithiocarbamate) monomer **1g**.[17] The monomer **1g** was purified using column chromatography with hexane/chloroform (50/50) as an eluent.

Synthesis of the ^{13}C-Labeled O-PTV Precursor Polymer (1h). The optimized polymerization route toward the precursor polymer has been reported earlier.[32,37] The polymerization of the precursor polymers has been accomplished under influence of sodium bis(trimethylsilyl)amide (NaHMDS) (Scheme 1). Several precursor polymer batches were prepared and fractionated by means of reversed precipitation in order to separate the low from the high molecular weight fractions toward characterization by GPC and quantitative NMR (see later in the characterization part). After fractionation the amounts of precursor polymers **1A**, **1B**, and **1C** were too low to allow a comparative study of the acid and thermally induced conversion to the conjugated state. Therefore, a larger batch of precursor polymer has been prepared of which the high molecular weight fraction (**1D**) was divided into two parts. It can be noted that the higher the amount of starting monomer used for the polymerization, the higher the molecular weight of the high molecular weight fraction (see also Experimental Section) appears to be.

Table 2. Chemical Shift Assignment of the Proton and Carbon NMR Signals of Precursor O-PTV

carbon atom	chemical shift ^{13}C (ppm)	T_{1C} (s)	chemical shift ^{1}H (ppm)
C1/C2	12.3/13.4		1.05−1.40
C3/C4	47.4/49.8		3.66/3.96
C5	194.7		
C6	53.3		5.35
C7	37.2		3.17
C8/C11/C9	134.4/139.3/140.2		
C10	128.4		6.49
C12	29.0	0.21	2.28
C13	31.6	0.41	1.05−1.40
C14/C15	30.4	0.52	1.05−1.40
C16	30.1	0.76	1.05−1.40
C17	32.7	1.32	1.05−1.40
C18	23.4	1.85	1.05−1.40
C19	14.9	2.80	0.85

Synthesis of the ^{13}C-Labeled O-PTV (1i). To investigate and compare two different conversion mechanisms toward the conjugated state in more detail, the large batch of precursor polymer (**1D**) has been divided in two equal parts of which one part was converted thermally while a smoother acid induced method was used for the other part (Scheme 1).[38] The resulting O-PTV polymers were studied by quantitative NMR spectroscopy.

Characterization of the ^{13}C-Labeled Precursor Polymer. The first step in the polymerization pathway is the formation of the actual monomer, a quinodimethane system (Scheme 2), by a base-induced 1,6-elimination from the premonomer. Then, a self-initiating radical polymerization reaction is triggered by the recombination of two quinodimethane systems yielding the initiating species, a diradical.[39,40] In this way intrinsic defects can be formed in the central part of the precursor polymer. Consequently, the propagation occurs by addition of quinodimethane systems on both sides of the initiator. Because of the nonsymmetric nature of the monomer, three different ways of

monomer addition can take place for the growing polymer chain. More specific, next to the normal head-to-tail addition which will lead to the formation of double bonds upon conversion to the conjugated state, head-to-head and tail-to-tail additions can take place, which are considered as structural defects.[41−44]

In order to identify and quantify the amount of structural defects present in the main chain, four different ^{13}C-enriched O-PTV precursors were studied by ^{13}C NMR (**1A**, **1B**, **1C**, **1D**) of which the molecular weights are listed in Table 1.

Figure 1 presents the chemical structure and carbon numbering for precursor O-PTV.

Analysis of the proton-decoupled ^{13}C spectrum, DEPT and INADEQUATE experiments allowed us to assign the NMR signals as presented in Table 2. The chemical shift assignment of the carbon nuclei of the octyl side chain is based on the T_{1C} relaxation decay times. For mobile side chains it can be stated that the closer the carbon is situated toward the side chain end, the longer its relaxation decay time will be due to less restricted conformational motions.

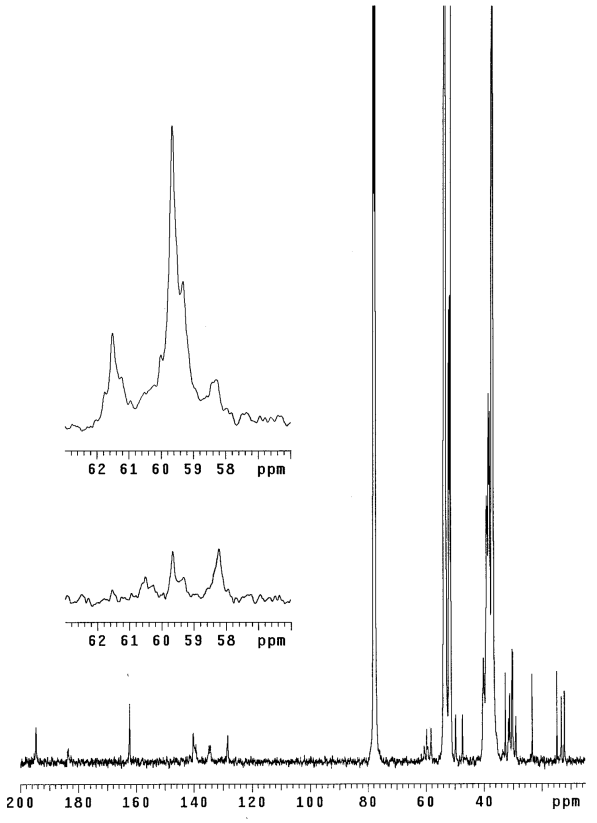


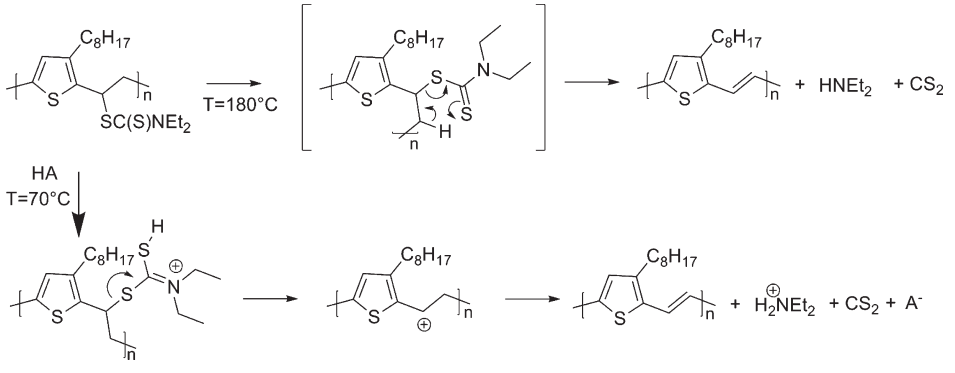
Figure 2. ^{13}C NMR spectrum of precursor polymer **1D** (top inset = polymer **1A**, bottom inset = polymer **1D**).

However, next to the signals described in Table 2, some remaining carbon signals were detected in the ^{13}C spectra (Figure 2). On the basis of their intensities, these signals have to arise from ^{13}C-labeled carbons situated in end groups or in structural defects in the main chain. The carbonyl signals around 183.5 and 162.3 ppm do not show a $^{1}J_{C-C}$ coupling and therefore have to represent end groups. Table 1 shows a decrease in their intensity with increasing M_n, confirming that it concerns end-group signals. DEPT spectra indicate that the 162.3 ppm signal originates from a quaternary carbon while the 183.5 ppm signal represents a methine carbon. The resonances at 59.7 and 61.5 ppm are methylene carbons (DEPT) and show the same trend; i.e., their intensity increases with decreasing molecular weight (see insets of Figure 2), and no $^{1}J_{C-C}$ coupling is observed. The assignment of these end-group signals to aldehyde (183.5 ppm), carboxylic acid (162.3 ppm), and methylol (59.7 and 61.5 ppm) functional groups will be discussed later on. By means of quantitative ^{13}C NMR spectroscopy, the amount of all end groups was determined, and the number of repetition units was calculated and compared to that obtained by GPC as presented in Table 1. As the GPC measurements are calibrated against polystyrene standards, it is not unusual that the GPC results show an overestimation of the molecular weights.

Characterization of the ^{13}C-Labeled Conjugated O-PTV. The thermal conversion of the precursor polymer to the conjugated state can be accomplished by heating a solution of precursor O-PTV in dichlorobenzene at a typical temperature of 180 °C. The mechanism is presented below as a concerted mechanism although a stepwise (radical) mechanism cannot be excluded (Scheme 3). However, since these high temperatures may lead to thermal degradation, an acid-induced conversion method has been developed that allows to convert the precursor O-PTV at much lower temperatures (typically 70 °C).[38]

At first glance the NMR spectra of the converted polymers seem to be very similar (Figures 3 and 4). The ^{13}C spectra indicate that the polymer is fully converted; i.e., no trace of the signal of the C6 carbon bearing the dithiocarbamate group (53.3 ppm) is detected anymore, and the resonance characteristic of the double bond appears around 120 ppm. The resonances at 183.5, 162.3, 61.5, and 59.7 ppm are still present in the ^{13}C NMR spectrum which confirms their assignment to end groups. The amount of end groups is presented in Table 1. Two independent characterization techniques, i.e., GPC and NMR,

Scheme 3. Thermal- and Acid-Induced Conversion of Precursor O-PTV



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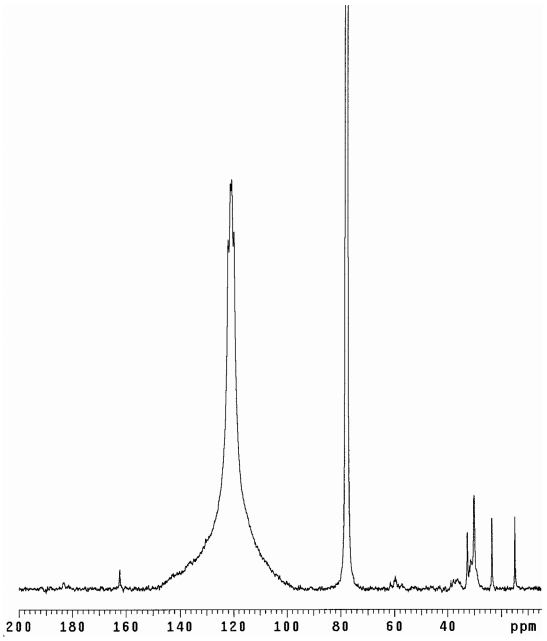


Figure 3. ^{13}C NMR spectrum of the acid converted O-PTV.

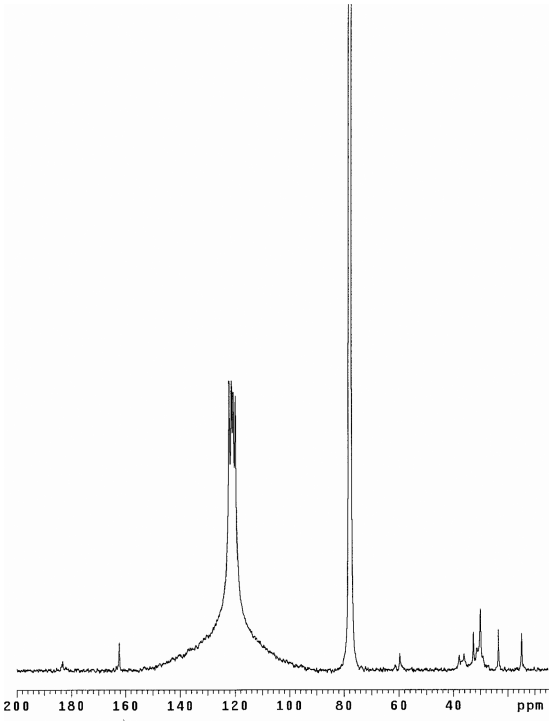


Figure 4. ^{13}C NMR spectrum of the thermally converted O-PTV.

demonstrate that the average number of repetition units is higher in acid converted O-PTV as compared to thermally converted O-PTV. Note that the higher M_n found for acid converted O-PTV, as compared to the O-PTV precursor, can be explained by a difference in hydrodynamic volume for GPC and an error margin of around 0.3% for the NMR quantification. It can be concluded from these molecular weight data that starting from the same batch of precursor polymer the thermal conversion to

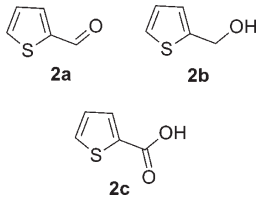


Figure 5. Model compounds for end groups.

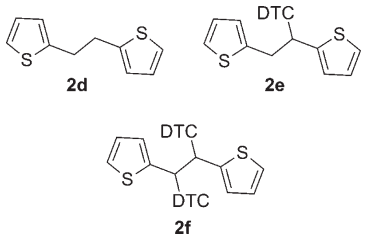
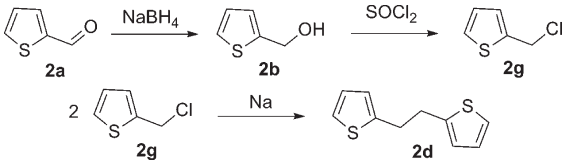


Figure 6. Model compounds for possible structural units in the precursor polymer.

Scheme 4. Synthesis of Model Compound 2d



the conjugated polymer is accompanied by a chain scission process which does not occur or to a lesser extent for the acid-induced conversion process. Most probably the high temperature (180 °C) induces chain scission at the weakest points in the polymers structure, i.e., at the head-to-head defects.

Identification of End Groups and Structural Defects. *End Groups*. While the ^{13}C chemical shifts of the signals at 183.5 and 162.3 ppm are pointing to aldehyde and carboxylic end groups, the chemical shifts at 61.5 and 59.7 ppm point to methylol end groups. In order to confirm this assignment, model compounds **2a**, **2b**, and **2c** (Figure 5) have been fully characterized by NMR (see Experimental Section).

The assignment of the resonance at 183.5 ppm to an aldehyde group is confirmed by means of the model compound **2a**. Further oxidation toward a carboxylic acid would not be unexpected. Model compound **2c** shows a resonance at 168.8 ppm which confirms the assignment of the 162.3 ppm resonance to a carboxylic acid function. The methylol model compound **2b** was synthesized and presents a ^{13}C resonance at 59.3 ppm, which allows to assign the signals at 59.7 and 61.5 ppm to methylol end groups.

Structural Defects. With the end groups and regular head-to-tail polymer signals determined, only some very small signals remain undefined, i.e., a signal for the precursor polymer at 58.2 ppm and two for the conjugated polymer around 36−38 ppm (remark that the chemical shift difference is too large to assign them to a doublet as a result of $J_{13C-13C}$ coupling). Since the intensity of these undefined signals, arising from ^{13}C-labeled carbons, is very small, it demonstrates that the amount of structural head-to-head and tail-to-tail polymerization defects has to be very small.

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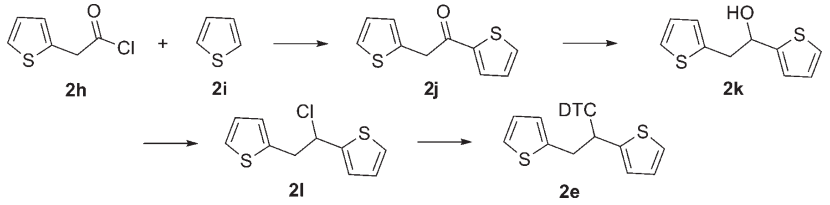
Scheme 5. Synthesis of Model Compound 2e



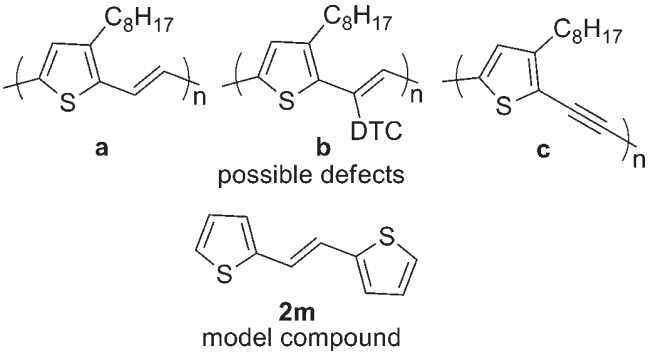


Figure 7. Additional structural units possible in O-PTV (**a**, **b**, **c**) and model compound for a head-to-tail unit after conversion (**2m**).

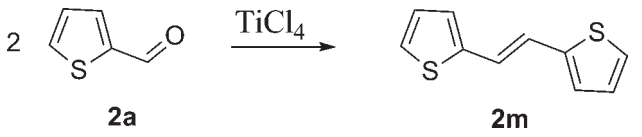
To get chemical shift information regarding the possible structural units in the precursor and conjugated polymers, several model compounds have been made. Toward the identification of structural defects at the precursor polymer level, two different model compounds **2d** (for head-to-head coupling) and **2e** (for normal head-to-tail) have been synthesized (Figure 6). The synthesis of model compound **2f** for the tail-to-tail coupling has been explored extensively, but without success. The first model compound **2d** has been synthesized by the well-known Wurtz coupling of 2-(chloromethyl)thiophene, **2g** (Scheme 4).[45] This chloride **2g** has been made by a two step synthesis from 2-thiophene carbaldehyde, **2a**. After a reduction with $NaBH_4$, the alcohol **2b** has been converted into the chloride **2g** by $SOCl_2$.[46]

The second model compound **2e** has been synthesized by a four-step pathway (Scheme 5). After a Friedel−Crafts reaction between 2-thiopheneacetyl chloride (**2h**) and thiophene (**2i,**) the resulting keton **2j** has been reduced to the alcohol **2k** by $NaBH_4$ in an almost quantitative yield.[47] In a next step the alcohol **2k** was transformed into a rather unstable chloride **2l** which was immediately converted into model compound **2e** via a substitution reaction with diethyldithiocarbamic acid sodium salt.[17,46]

Three additional structural units can appear at the level of the conjugated O-PTV (Figure 7). The model compound **2m** contains the double bond present in the structural unit obtained upon elimination of a normal head-to-tail unit. This model compound has been synthesized by a McMurry coupling of 2-thiophene carbaldehyde **2a** under influence of Zn and $TiCl_4$ (Scheme 6).[47] The elimination of dithiocarbamate groups out of a tail-to-tail structural unit can lead to defects as presented in Figure 7 for a partial elimination (**b**) and double elimination (**c**). The latter would show a triple-bond resonance signal that would be easily observed in the ^{13}C NMR spectra around 90 ppm and which is not detected.

Regarding the undefined signal at 58.2 ppm in the ^{13}C spectrum of the precursor polymer, its relative intensity is not influenced by the molecular weight. This suggests that the corresponding carbon atom resides in the main chain. However, since the signal appears as a singlet, the corresponding ^{13}C atom should be linked to a chemically identical ^{13}C atom, explaining why no J_{C-C} coupling is observed. It can be expected that C6/C7 of a tail-to-tail addition would have a resonance at this position (Figure 8). Moreover, the observations that (a) DEPT spectra indicate that this signal corresponds to a CH group and (b) this signal disappears in the conjugated polymer are strong indications to assign the resonance at 58.2 ppm to a tail-to-tail defect.

Scheme 6. Synthesis of Model Compound 2m



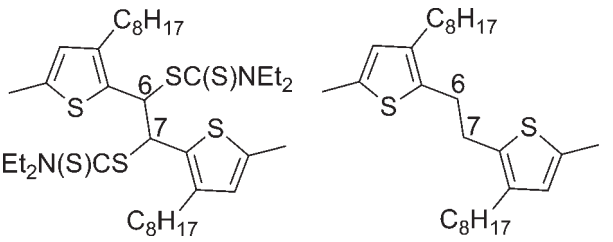


Figure 8. Chemical structure of tail-to-tail (left) and head-to-head (right) defects in precursor O-PTV.

The model compound **2d** shows a methylene signal at 32.8 ppm. Since no signal was detected at this position in the ^{13}C spectrum of the precursor polymer, no direct evidence for head-to-head defects was found at the precursor level. It can however not be excluded that the position of this methylene signal is slightly shifted downfield in the precursor polymer and so would end up in the foot of the huge C7 signal (37.2 ppm) of the normal head-to-tail units. The ^{13}C spectrum of converted O-PTV (see below) should make this clear.

The chemical shifts of the bridge methylene and methine carbon resonances of model compound **2e** (38.8 and 52.9 ppm) are in good agreement with those of C7 and C6 in normal head-to-tail units of the precursor O-PTV (37.2 and 53.3 ppm).

Regarding the two undefined signals in the ^{13}C spectrum of the conjugated polymer at 36−38 ppm, DEPT spectra indicate that these resonances correspond to CH_2 groups. These methylene signals might arise from units of incomplete elimination (represented by model compound **2e**) or from head-to-head defects (represented by model compound **2d**). However, incomplete elimination can be excluded since no signal appears

from the dithiocarbamate group bearing methine carbon around 53.3 ppm. Moreover, since no $J_{13C-13C}$ coupling is observed, these resonances are assigned to head-to-head defects. As discussed above, these resonances were not observed for the precursor O-PTV as they were masked by the huge C7 signal of normal head-to-tail structural units.

Regarding the 58.2 ppm signal in the precursor spectrum, assigned to tail-to-tail defects, no characteristic signal of a triple bond is detected in the spectra of the converted polymers (around 90 ppm). This indicates that no full elimination of the tail-to-tail defects occurs, leaving a structural unit as indicated in Figure 7 (**b**) of which the carbon signals will end up in the huge signal of the ^{13}C-labeled olefinic carbons of the normal head-to-tail units.

The amount of defects has been calculated from the ^{13}C NMR spectra. For the head-to-head defects, measured via the spectra of O-PTV, an amount of 0.6% is found. These defects are most probably responsible for chain scission on thermal conversion. The amount of tail-to-tail defects, measured via the spectrum of the precursor O-PTV, is rather similar, i.e., in the order of 0.6%. Therefore, it can be definitely concluded that the dithiocarbamate precursor route is an excellent route toward PTV-based polymers with a very low amount of structural defects.

Last but not least, the ^{13}C NMR spectra clearly demonstrate that the relative intensity of the methylene carbon signal of head-to-head defects ($2 \times 0.6\%$) is much smaller than this of the carbons in end groups. This indicates that the initiation unit of the polymerization reaction cannot be a head-to-head unit solely, as the amount of carbons in end groups and in methylene groups of head-to-head units should than be identical. For substituted PTVs prepared via the DTC route, it can be expected that toward the formation of the actual monomer, the long octyl side chains will stimulate the base to abstract an acid proton at the opposite site of the premonomer due to steric hindrance (Scheme 2).[48] During the next initiation step, two of these *p*-quinodimethane systems can than combine in three different ways of which the head-to-tail initiation seems to be preferential. This can explain the low amount of head-to-head (and tail-to-tail) structural units in these polymers.

CONCLUSIONS

This study describes an extensive structural characterization of ^{13}C-labeled 3-octyl-PTV and its precursor polymer, prepared via the dithiocarbamate route, by means of several NMR techniques and model compounds. Aldehydes, carboxylic acids, and methylol groups have been detected as polymerization end groups. It is further demonstrated that the dithiocarbamate precursor route is an excellent route toward PTV-based polymers with a minor amount of structural defects; i.e., head-to-head and tail-to-tail structural defects are found in an amount as low as 0.6%. This probably because, due to steric constraints caused by the side chains, the head-to-tail initiation is preferential in the polymerization reaction of substituted PTV derivatives. Last but not least, with respect to the conversion of the precursor polymer to its conjugated state, it is shown that thermal degradation can be avoided by using a smooth, acid-induced elimination procedure.

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