Synthesis of poly(2,5-Thienylene Vinylene) and its derivatives: Low band gap materials for photovoltaics

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Abstract

Poly-(2,5-Thienylene Vinylene) (PTV) derivatives have been synthesised *via* the "dithiocarbamate precursor route" in good yield and satisfactory molecular weight. Structural characterisations of the conjugated PTV polymers reveal an optical band gap around 1.8 eV. Organic field effect transistors and organic based photovoltaic devices were made with the plain PTV, *via* a precursor approach. More specifically, solar cells were produced using a blend of the precursor PTV polymer and PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C_{61}) at various ratios, converted *in situ* in thin film. A promising power efficiency of 0.76% was achieved.
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1. Introduction

Conjugated polymers are of a great interest for development of optical and electronic applications because of their extended π-electron delocalisation along the backbone. A problem however in the synthesis of conjugated polymers is their insolubility due to their rigid backbone. Quite often the solubility problem is circumvented by the use of a soluble and easy processable non-conjugated precursor polymer. Nowadays, such precursor polymers can be synthesised *via* four different routes: the dehalogenation or Gilch route [1], the sulphonium or Wessling–Zimmerman precursor route [2,3], the xanthate precursor route [4] and the sulphinyl precursor route [5–7] (Scheme 1). These four routes have in common that they make use of polymerisation behaviour of *p*-quinodimethane

systems. They differ however in the choice of the leaving group (L) and polariser group (P) in the premonomer structure and the polymerisation conditions (base and solvents used, reaction temperatures and reaction time). Initially these methods were developed for the synthesis of poly (*p*-phenylene vinylene) (PPV) derivatives and were later adapted for the synthesis of other poly (heteroarylene vinylene)s, but with mixed results.

Especially the synthesis of electron rich conjugated polymers as poly (2,5-Thienylene Vinylene) *via* these precursor routes is problematic. Despite the fact that Harper and Watson [8] patented the Wessling route towards PTV, it was when Elsenbaumer et al. [9–11] polymerised 2, 5-bis (tetrahydrothiophenonium methyl) thiophene dichloride in water, that research towards PTV accelerated. The precursor polymer obtained was not stable, spontaneous elimination to the unprocessable PTV occurred. Saito et al. [12–15] and Murase et al. [16,17] independently reported on the synthesis of a precursor polymer bearing methoxy leaving groups. This polymer precipitated from the reaction mixture when the water-soluble sulphonium precursor was treated with methanol. This precursor was soluble in organic solvents, which was favourable for the characterisation and processability

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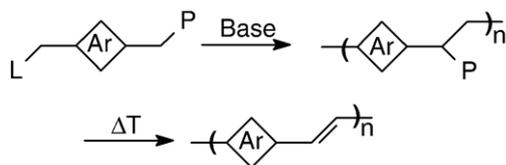
Scheme 1. Synthesis routes towards poly(arylene vinylene)s: Wessling–Zimmerman: L = P = $^{\oplus}SR_2$; Gilch: L = P = Cl; Xanthate: L = P = SC(S)OR; Sulphinyl: L = Cl, P = S(O)R.

of the polymer. Later, Eevers et al. [18,19] and Xie et al. [20] reported on a preparation method for PTV from a methoxy precursor polymer. In 1989, Iwatsuki et al. [21] described an alternative method to prepare a film of fully conjugated PTV by a dehydrogenation reaction in dioxane from a poly (2,5-thienylene ethylene) (PTE) film using 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ) as an oxidising reagent and more recently, Herwig et al. [22] patented a method involving the polymerisation of 2, 5-bisthioalkylmethylthiophenes. However all these routes suffer from one or more drawbacks, e.g. the need to use HCl gas to promote conversion or the use of an additional reagent for post-polymerisation modification. Furthermore until recently, the high reactivity of intermediates or even the monomer itself, precludes the development of a reproducible, versatile and high yield polymerisation process toward PTV derivatives. This relates to the electron rich nature of the thiophene ring. For example, in our research group [23–25] the development of the synthesis of PTV via the sulphinyl precursor route was started, but instability of the intermediary products toward the corresponding sulphinyl monomer precluded good results. Consequently we started a study of another precursor route, which could hold the promise of a stable monomer structure: the xanthate precursor route. Both in our research group [25] and by Burn et al. [26] it was found that the xanthate precursor route could be used to synthesise PTV. Drawbacks however, in the use of this method were the rather low yield and the high polydispersity (PD > 15) of the obtained polymers. Also a shift to lower wavelength of the maximum absorption λ_{max} of the polymer so obtained ($\lambda_{max} < 540$ nm) compared to literature [9] ($\lambda_{max} = 600$ nm) could be observed. This was interpreted as an indication for the presence of structural chemical defects in the backbone of the conjugated polymer. Independently we [25] and Padmanaban et al. [28] considered the use of a dithiocarbamate functional group as a potential precursor for a double bond. In the latter case a PPV-precursor was synthesised by competitive nucleophilic substitution of the Wessling polyelectrolyte with the respective nucleophile, sodium diethyl dithiocarbamate. Detailed studies of the thermal-elimination kinetics of the dithiocarbamate precursor, both in solution and in thin films, were carried out by in situ monitoring of their ultraviolet visible spectra. We could obtain a similar precursor polymer by base induced polymerisation of a bis-dithiocarbamate derivative of the corresponding monomer [27,29]. In this paper the use of the dithiocarbamate precursor route toward the synthesis of PTV's will be presented. As will be demonstrated this precursor route allows for the synthesis of the low band gap polymer, PTV, with low polydispersity, low chemical defect content and in good yield. Also the use of said precursor material

to produce efficient photovoltaic devices will be discussed. An effort to use the same protocol to obtain 3- and 3,4-alkylated PTV's however failed.

2. Experimental details

2.1. Materials

Tetrahydrofuran (THF) used in the synthesis was refluxed under nitrogen with sodium metal and benzophenone until a blue colour persisted, all the commercially available chemicals were purchased from Acros or Aldrich and were used without further purification unless stated otherwise.

2.2. Techniques

^{1}H NMR (proton Nuclear magnetic Resonance) spectra were taken on a Varian Inova 300 spectrometer. For all synthesised compounds, spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm relatively to TMS (tetramethyl-silane) was used as reference.

Average molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by Size Exclusion Chromatography (SEC). Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10 μm, 2×30 cm, Polymer Labs) and a relative index (RI) detector (Shodex) at 70 °C. A dimethylformamide (DMF) solution of oxalic acid (1.1 10^{-3} M) was used as the eluent at a flow rate of 1.0 mL/min. Toluene was used as flow rate marker.

Gas chromatography/mass spectometry (GC/MS) analyses were carried out at the TSQ-70 and Voyager mass-spectrometers (Thermoquest), capillary column: Chrompack Cpsil5CB or Cpsil8CB.

Fourier transform infrared spectroscopy (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer. Samples for the FT-IR characterisation were prepared by spin-coating the precursor polymer from a chloroform solution (6 mg/mL) onto NaCl disks at 500 rpm. The NaCl disks were heated in a Harrick oven high temperature cell (purchased from Safir), which was positioned in the beam of the FT-IR to allow in situ measurements. The temperature of the sample and the heating source were controlled by a Watlow temperature controller. The heating source was in direct contact with the NaCl disk. Spectra were taken continuously and the heating rate was 2 °C/min from room temperature up to 350 °C. The atmosphere in the temperature cell could be varied from a continuous flow of nitrogen to vacuum (15 mm Hg). Timebase software was used to investigate regions of interest.

Ultraviolet visible spectroscopy (UV–Vis) was performed on a VARIAN CARY 500 UV–Vis–NIR spectrophotometer. The precursor polymer was spin-coated from a chloroform solution (6 mg/mL) onto quartz glass at 700 rpm. The quartz glass was heated in the same Harrick oven high temperature cell as was used in the FT-IR measurements. The cell was placed in the beam of the UV–Vis spectrophotometer, which was specially adapted to harbour the high temperature cell and spectra were

taken continuously. The heating rate was 2 °C/min up to 350 °C. All measurements were performed under a continuous flow of nitrogen. Scanning kinetics software was used to investigate the regions of interest.

Thin film electrochemical properties were measured with an Eco Chemie Autolab PGSTAT 20 Potentiostat/Galvanostat using a conventional three-electrode cell (electrolyte: 0.1 mol/L tetra-*n*-butylammoniumhexafluorophosphate (TBAPF6) in anhydrous CH_3CN) with an Ag/Ag^+ reference electrode (0.01 mol/L $AgNO_3$, 0.1 mol/L $LiClO_4$ and CH_3CN), a platinum counter electrode and an indium-tin oxide (ITO) coated glass substrate as working electrode. Cyclic voltammograms were recorded at 50 mV/s under N_2 atmosphere. All electrochemical potentials have been referenced to a known standard, ferrocene/ferrocinium, which in acetonitrile solution is estimated to have an oxidation potential of −4.98 eV *vs.* vacuum.

The glass transition temperature (T_g), was measured by Differential Scanning Calorimetry (DSC) on a DSC 2920 of TA instruments. The heating rate was 20 °C/min and the N_2 flow was 40 mL/min. T_g was taken as the midpoint of the inflection tangent.

A Bruker D8 Discover diffractometer equipped with a Göbel mirror (copper target-$K_{\alpha 1}$ and $K_{\alpha 2}$ lines) and centric cradle was used to obtain 1-D X-ray diffraction (XRD) profiles. The spectra were taken under a step-scan rate of 0.04 ° per 40 s in the scattering angle range of $2\theta = 2°–50°$.

2.3. Synthesis of 2,5-bis(hydroxymethyl)-thiophene (2a)

In a 100 mL round-bottom flask was added $LiAlH_4$ (0.38 g, 10 mmol) to dry THF (50 mL, dried over sodium) under argon atmosphere. This slurry was cooled to 0 °C and the diester **1a** (1 g, 5 mmol) was slowly added portion wise. When the addition was completed a reflux condenser was fitted and the slurry was heated at reflux temperature for 2 h. During this time a grey, concrete-like substance was formed that was hard to stir. After cooling down, air was allowed to get in the system and the reaction mixture was placed in an ice bath. Then, it was quenched by cautious sequential addition of water, aqueous 15% NaOH solution, and again water until no more gas development could be detected. This solution was filtered and the residue was extracted with ether. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The diol **2a** was obtained as yellowish oil (0.65 g, 91%). ^{1}H NMR ($CDCl_3$): δ(ppm) 6.73 (2H), 4.62 (4H), 3.57 (2H). MS (EI, *m/z*, rel. int. (%)): 144 ([M]$^+$, 78), 113 ([M−CH_2OH]$^+$, 100), 82 ([M−2× CH_2OH]$^+$, 74).

2.4. Synthesis of 2,5-bis(chloromethyl)-thiophene (3a)

To a cooled (0 °C), stirred solution of diol **2a** (0.9 g, 5 mmol) in THF (20 mL) was slowly added a solution of $SOCl_2$ (0.9 mL, 1.49 g, 12.5 mmol) in THF (5 mL). The temperature of the reaction mixture was allowed to increase to room temperature (R.T.) under continuous stirring for 1 h. Then, the mixture was cooled down again at 0 °C and a saturated sodium carbonate

solution was added dropwise until neutral. The mixture was extracted with ether and dried over $MgSO_4$. The solvent was evaporated and the highly reactive dichloride **3a** was obtained as a yellow oil.

2.5. Thiophene-2,5-diylbismethylene N,N-diethyl dithiocarbamate (4a)

To a solution of bischloromethyl (0.7 g, 4 mmol) **3a** in ethanol (10 mL), sodium diethyldithiocarbamate trihydrate (or diethyldithiocarbamic acid sodium salt trihydrate) (5 g, 12 mmol) was added as a solid. The mixture was stirred at ambient temperature for 2 h. Then, water was added and the desired monomer was extracted with ether (3×100 mL) and dried over $MgSO_4$. Evaporation of the solvent yielded (81%) of the pure product as a white solid used as it is. ^{1}H NMR ($CDCl_3$): 6.84 (s, 2H), 4.69 (s, 4H), 4.01 (q, *J*=7.2 Hz, 4H), 3.69 (q, *J*=7.2 Hz, 4H), 1.26 (t, *J*=7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$): 194.29, 138.76, 126.77, 49.46, 46.70, 36.72, 12.46, 11.53; MS (EI, *m/e*): 258 (M$^+$−SC(S)NEt$_2$), 148 (SC(S)NEt$_2$).

2.6. Synthesis of 3-hexylthiophene (2b)

In a three-necked flask to a solution of 3-bromothiophene **1b** (1 g, 7.4 mmol) ether and NiCl2 1,3-bis(diphenylphosphino) propane (dppp) catalyst (5%), stirred under vacuum, the hexyl magnesium bromide (2.0 M in diethyl ether 7.4 mL, 37 mmol) was added dropwise *via* a cannula at 0 °C. After complete addition the mixture was stirred at R.T. over night. Then, the mixture was quenched with diluted HCl and extracted with dichloromethane; the organic layer was dried over $MgSO_4$ and the obtained product was purified *via* flash chromatography using hexane as eluent to give **2b** as colourless oil in a yield of 95%. 1H NMR (CDCl3): 7.3 (dd, 1H), 7.03 (m, 1H), 6.90 (d, 1H), 2.67 (t, 2H), 1.64 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H).

2.7. Synthesis of 3-hexyl-2,5-di-bromo-thiophene (3b)

In a round-bottom flask 3-hexylthiophene **2b** (1 g, 6 mmol) and DMF were stirred at 0 °C and a solution of *N*-bromossuccinimide (NBS) (2.3 g, 13 mmol) in DMF was added slowly *via* a dropping funnel (the concentration of 3-hexylthiophene in the final reaction mixture is 0.3 M). The mixture was stirred for 3 days at R.T. in the darkness. Then, the reaction mixture was poured onto an equal volume of ice and extracted with ether. The organic layer was washed afterwards with NaOH 2.5 M and saturated NaCl solution. The solvent was evaporated and the product listed in the title (**3b**) was obtained as a colourless oil (yield 82%). ^{1}H NMR (CDCl3): 6.74 (s, 1H), 2.50 (t, 2H), 1.53 (m, 2H), 1.32 (t, 6H), 0.84 (t, 3H).

2.8. Synthesis of 3-hexyl-2,5-thiophenedicarboxaldehyde (4b)

In a three-necked round-bottom flask 2,5-dibromo-3-hexylthiophene **3b** (1 g, 3 mmol) and THF (10 mL) were stirred under vacuum at −78 °C. A solution 1.6 M of *n*-butyllithium (*n*-BuLi) (4.1 mL, 6.6 mmol) was added slowly with a cannula,

the mixture was stirred for 30 min and afterwards 1-formylpiperidine, previously distilled, (0.76 g, 6.7 mmol) was slowly added. The reaction mixture was left at 25 °C under continuous stirring for 12 h. HCl 2 M was added to destroy the excess of BuLi followed by extraction with chloroform.

The oily compound obtained was purified *via* a column chromatography in silica gel, chloroform/hexane (5:5) and, yielded the di-aldehyde as orange oil (96%). ^{1}H NMR (CDCl$_3$): ^{1}H NMR (CDCl$_3$): 10.02 (s, 1H), 9.98 (s, 1H), 7.6 (s, 1H), 3.0 (t, 2H), 1.67 (m, 2H), 1.34 (m, 6H), 0.84 (t, 3H).

2.9. Synthesis of 3-hexyl-2,5-bis(hydroxymethyl)thiophene (5b)

As described in **2a**. The pure diol **5b** was obtained as yellowish oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): 6.75 (1H), 4.41 (4H), 3.73 (2H), 1.84 (2H), 1.54 (2H), 1.24 (4H), 0.87 (3H).

2.10. Synthesis of 3-hexyl-2,5-bis(chloromethyl)thiophene (6b)

As described in **3a**.

2.11. Synthesis of thiophene 3-hexyl-2,5-diylbismethylene N,N-diethyl dithiocarbamate (7b)

As described in **4a**. The monomer was obtained as yellow oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): 6.75 (s, 1H), 4.65 (s, 2H), 4.58 (s, 2H), 4.04 (q, 4H), 3.73 (q, 4H), 1.52 (m, 2H), 1.27 (m, 20H), 0.87 (t, 3H).

2.12. Synthesis of 3,4-dihexylthiophene (2c)

Hexyl magnesium bromide (2.0 M in diethyl ether 12 mL, 62 mmol) was added dropwise *via* a cannula to a stirred solution of 3,4-dibromothiophene **1c** (3 g, 12 mmol) and NiCl$_2$ (dppp) catalyst (5%) in ether, under vacuum, at 0 °C. After complete addition the mixture was refluxed for 20 h. It was then cooled down again at 0 °C and quenched with diluted HCl. The mixture was extracted with dichloromethane; the organic layer was dried over MgSO$_4$ and the product obtained after evaporation of the solvent was purified *via* flash chromatography in hexane to give the pure 3,4-dihexylthiophene as colourless oil in a yield of 95%. ^{1}H NMR (CDCl$_3$): 6.87 (s, 2H), 2.50 (t, 4H), 1.64 (m, 4H), 1.31 (m, 12H), 0.90 (t, 6H).

2.13. Synthesis of 3,4-dihexyl-2,5-dibromo-thiophene (3c)

In a round-bottom flask 3,4-dihexyl-thiophene **2c** (3.2 g, 12 mmol) and a mixture of chloroform/acetic acid 50:50 (50 mL) were stirred and heated to 30 °C; NBS (4.48 g, 25.2 mmol) was slowly added. After complete addition, the reaction mixture was refluxed for 15–20 min, then cooled down again and diluted with an equal volume of water, the chloroform layer was separated and washed (3 times) with sodium carbonate solution and once with water. The dibromo derivative **3c** was obtained as a yellowish oil (yield 90%). ^{1}H NMR (CDCl$_3$): 2.51(t, 4H), 1.31 (m, 12H), 0.89(t, 6H).

2.14. Synthesis of 3,4-dihexyl-2,5-thiophenedicarboxaldeyde (4c)

In a three-necked round-bottom flask 3,4-dihexyl-2,5-dibromothiophene **3c** (4.79, 11.7 mmol) and THF were stirred under vacuum at −78 °C. A solution 1.6 M of *n*-BuLi (16.1 mL, 25.74 mmol) was slowly added *via* a cannula and stirred for 30 min. 1-formylpiperidine, previously distilled, was added (2.92 g, 25.8 mmol), and the reaction mixture was stirred at 25 °C for 12 h. HCl 2 M was added to quench the excess of BuLi followed by extraction with chloroform. The mixture was purified *via* column chromatography with chloroform/hexane (5:5) used as eluent and the pure product was obtained as orange oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): 10.09 (s, 2H), 2.9(t, 4H), 1.55 (m, 4H), 1.31 (m, 12H), 0.87 (t, 6H).

2.15. Synthesis of 3,4-dihexyl-2,5-bis(hydroxymethyl)thiophene (5c)

As described in **2a**. The pure diol **5c** was obtained as yellowish oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): 4.73(s, 4H), 2.5 (t, 4H), 1.29 (m, 12H), 0.89 (t, 6H).

### 2.16. Synthesis of 3, 4-dihexyl-2, 5-bis (chloromethyl) thiophene (6c)

As described in **3a**.

2.17. Synthesis of thiophene 3,4-dihexyl-2,5-diylbismethylene N,N-diethyl dithiocarbamate (7c)

Compound **6c** was converted *in situ* in the diethyl dithiocarbamate monomer as described in **4a**. The pure monomer was obtained after purification *via* a column chromatography in ether as orange–red oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): 4.56 (s, 4H), 3.98 (s, 4H), 3.66 (q, 4H), 2.45 (q, 4H), 1.33 (t, 12H), 0.84(t, 6H).

2.18. Polymerisation

A solution of monomer (**4a** or **7b** or **7c**) in dry THF (the monomer concentration was set at 0.2 M) was degassed by passing through a continuous nitrogen flow. Monomers **7b** and **7c** were previously freeze dried. Lithium diisopropyl amide (LDA) (2 M solution in THF/*n*-hexane) was added in one go to the stirred monomer solution. The mixture was kept either at −78 °C, or room temperature or 0 °C, for 90 min under continuous nitrogen flow. The solution was then allowed to come to 0 °C. When the reaction temperature is −78 °C firstly ethanol (6 mL) is added to stop the reaction. The polymer was precipitated in ice water and the water layer was neutralized with diluted HCl then, extracted with chloroform. The solvent of the combined organic layers was evaporated under reduced pressure and a second precipitation was performed in a 1/1 mixture (100 mL) of diethyl ether and hexane at 0 °C in the case of **4a** or, pure cold methanol for **7b** and **7c**. The polymer was collected and dried *in vacuo*. ^{1}H NMR (CDCl$_3$) **5a**: 6.56–6.72
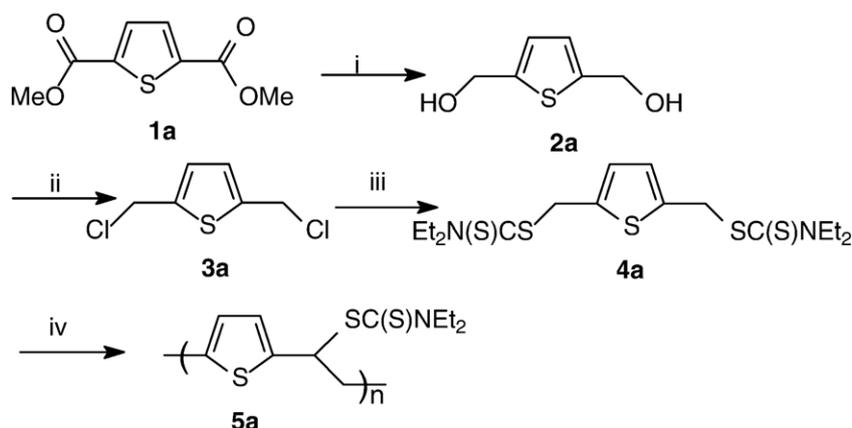
Scheme 2. Synthesis of dithiocarbamate monomer **5a**: i) LiAlH$_4$, THF; ii) SOCl$_2$, THF; iii) NaSC(S)NEt$_2$.3H$_2$O; iv) LDA, THF.

(br s, 1H), 6.72–6.36 (br s, 1H), 5.22–5.55 (br s, 1H), 3.81–4.12 (br q, 2H), 3.48–3.81 (br q, 2H), 3.11–3.40 (br s, 2H), 1.01–1.37 (br t, 6H). ^{13}C NMR (CDCl$_3$): 193.61, 140.77, 140.36, 126.15, 125.89, 52.50, 49.20, 46.73, 38.37, 12.45, 11.60. Elemental analysis: theoretical (C 51.32% H 5.87% N 5.44% S 37.36%), experimental (C 51.43% H 5.98% N 5.02% S 37.06%) ^{1}H NMR of **8b** and **8c** were not well resolved because the peaks relative to the monomer and side reaction products covered the peaks of the polymer.

2.19. Conversion reaction toward the conjugated polymer

The precursor polymer **5a** (300 mg) dissolved in dichlorobenzene (15 mL) was refluxed under stirring for 3 h. Then, the solvent was evaporated and, the slurry so obtained was precipitated in hexane. The precipitated was filtered off and washed several times with hexane.

3. Results

3.1. Monomer synthesis

The bis-dithiocarbamate thiophene monomer was synthesised from the commercially available dimethyl 2,5-thiophene-dicarboxylate **1a**, which was transformed into diol **2a** using LiAlH$_4$ (Scheme 2). Then 2,5-bischloromethylthiophene **3a** was obtained by reaction with thionylchloride (SOCl$_2$). Since the dichloride proved to be highly unstable, an *in situ* conversion towards the dithiocarbamate monomer was performed: the dichloride **3a** was dissolved in ethanol and sodium diethyl dithiocarbamate trihydrate was added to the reaction mixture as a solid to obtain **4a**.

The alkyl derivatives of PTV were prepared as described in Scheme 3. The monomers were obtained starting from the commercially available 3-bromothiophene (towards **7b**) or 3,4-dibromothiophene (towards **7c**). The Grignard reaction was carried out via a Kumada coupling [30] under vacuum and both the 3-hexylthiophene and the 3, 4-dihexylthiophene were obtained in a quantitative yield. The conversion of the 3-hexylthiophene **2b** to the 2,5-dibromo-3-hexylthiophene **3b** was very sensitive to the presence of light, which induces over

bromination of the alkyl side chain. In the formation of di-aldehyde **4b** and **4c**, special attention was given to the use of extreme dry reaction conditions in order to avoid the formation of large amounts of side products, *e.g.* mono-aldehyde. After the formation of the di-aldehyde the follow-up reactions were analogous to the ones described for PTV (Scheme 2). The obtained alkylated dithiocarbamate monomers **7a**, **b** behaved as hygroscopic oils.

3.2. Polymerisation towards the precursor polymers

The monomer **4a** was purified *via* a recrystallisation from ethanol/water (6/5). The use of strong base makes it necessary to freeze dry the monomer to eliminate any traces of water. The polymerisation of the thiophene dithiocarbamate monomers **4a**, **7b** and **7c** was performed in a three-necked flask. The monomer was dissolved in dried THF and degassed by passing through a continuous stream of nitrogen. The solution of base (2 M LDA solution in THF/*n*-hexane) was added in one go through a septum. Then, the reaction was stirred at a given temperature for 90 min under nitrogen atmosphere. The mixture was poured out in ice water. In case of a polymerisation temperature of −78 °C, the mixture was quenched before with ethanol instead of water. After extraction with chloroform, the combined organic layers were concentrated *in vacuo*. The crude product was dissolved in chloroform, precipitated in a 1/1 mixture of diethyl ether/*n*-hexane at 0 °C for **4a**, and in methanol for **7b** and **7c**, then collected and dried *in vacuo*. The polymerisation results are presented in Table 2. The molecular weights were determined by SEC with DMF as eluent. The polymerisation of **4a** leads only to low Mw polymers when one equivalent of base is used whatever the polymerisation temperature (Mw < 17,000 g/mol). The residual fraction shows after ^{1}H NMR analysis only unreacted monomer. High Mw PTV's are obtained when 2.0 equivalents of base is used in the polymerisation reaction (Mw ≅ 200,000). The residual fraction shows in that case the formation of side products beside some remaining monomer. The high Mw precursor polymer has a typical bimodal distribution that could be explained by the presence of two mechanisms taking place simultaneously during the polymer-isation process: (anionic and radical polymerisation) [31,32].
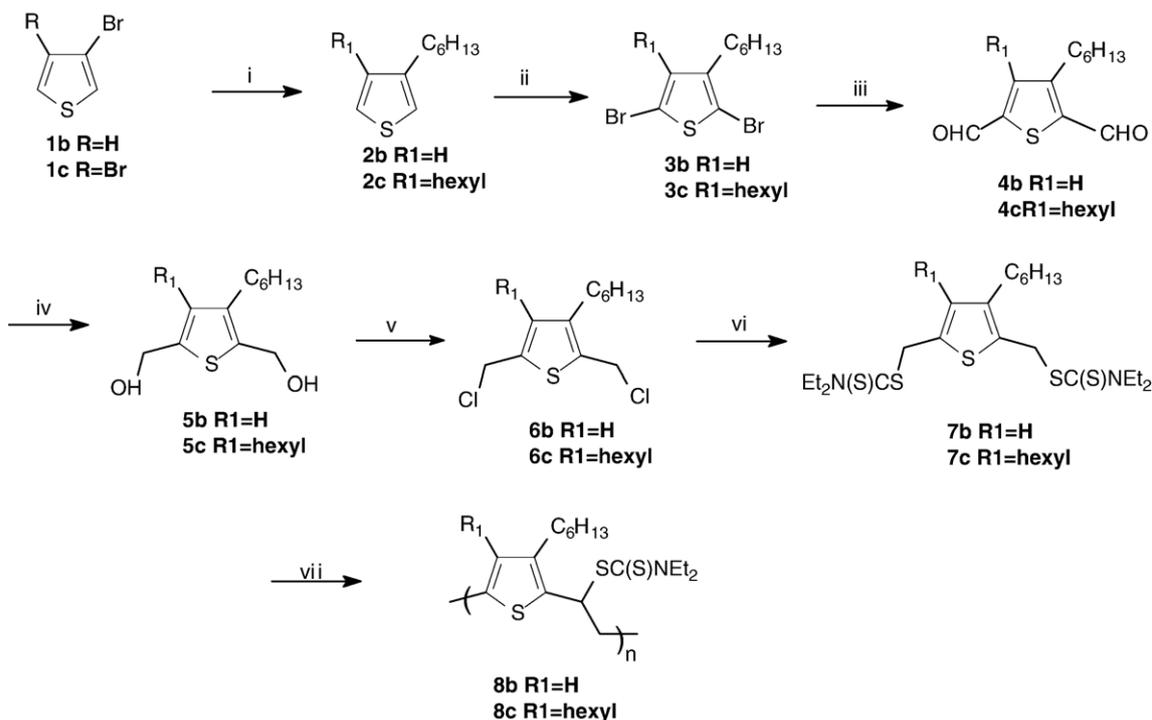
Scheme 3. Synthesis of dithiocarbamate monomer **7b** and **7c**: i) BrMgC$_6$H$_{13}$/NiCl$_2$(dppp); ii) b: NBS/DMF, c: NBS/CHCl$_3$/AcOH; iii) 1. BuLi, 2. formylpyperidine; iv) LiAlH$_4$, THF; v) SOCl$_2$, THF; vi) NaSC(S)NEt$_2$.3H$_2$O vii) LDA, THF.

Polymers with bimodal distribution of Mw were purified by preparative gel permeation chromatography (Bio-Beads® S-X exclusion limit of 14.000 Daltons)>> (Table 1). Going to higher concentration of base (3.0 equivalents), leads again to a decreased Mw, probably due to competing side reactions (Mw $\cong$ 70,000). However in this case all the monomer is consumed and the analysis of the residual fraction shows a very complex mixture of compounds.

The polymerisation of the alkyl substituted monomers **7b** and **7c** only leads to very low Mw polymers (Mw < 14,000) in low yield (< 5%). Side reactions are already occurring when one equivalent of base is used. The residual fractions were analysed by GC-MS and the main products formed are the results of the cleavage of the alkyl side chains on the thiophene rings. In some cases products are observed which imply the transfer of isopropyl groups from LDA, to the thiophene ring. The precise mechanism of such transfer reactions is not yet completely clear, but it can be assumed that it relates to the use of LDA as a base. The occurrence of such process on using LDA jeopardizes to a large extent the potential to synthesise soluble PTV derivatives by said precursor route.

3.3. Conversion of the precursors towards the conjugated PTV polymers

A precursor route has the advantage that in the case of a finally insoluble conjugated polymer as PTV, still, by thermal conversion of the soluble and processable precursor polymer, a high quality film of the conjugated polymer can be produced. The thermal elimination of the dithiocarbamate groups of the precursor

polymer as well as the thermal stability of the conjugated polymer was studied by means of *in situ* techniques. An *in situ* UV–Vis and a complementary *in situ* FT-IR study were carried out to deduct the conversion reaction protocol of the precursor polymers toward their conjugated forms. The reported UV–Vis and FT-IR spectra are representative for both the low and the higher Mw polymers, as they did not show significant differences in the conversion profiles.

When studying the thermal conversion to the conjugated structure from *in situ* UV–Vis spectroscopy, it was observed that the absorption maxima at R.T. of the conjugated polymers are shifted to longer wavelength (lower energy), compared to the polymers prepared *via* the xanthate route [25,26], a λ_{max} of 560 nm was detected [27] (Fig. 1). This points to an increased effective conjugation length of the π-electron system and thus is an indication of less structural defects in the backbone of the PTV obtained.

Only the polymers obtained *via* the polymerisation reaction at −78 °C showed an acceptable λ_{max} (Table 2). At 0 °C and at room temperature, polymers having significant lower λ_{max} were

Table 1
Molecular weight of polymer **5a** before and after preparative size exclusion chromatography

Before preparative SEC	After preparative SEC	
Mw (g/mol)	Mw (g/mol)	
Polymer **5a**	Fraction 1	Fraction 2
209.209	194.321	4.212
5.342		

a

b

Spectrum at R.T.

562 nm

640 nm
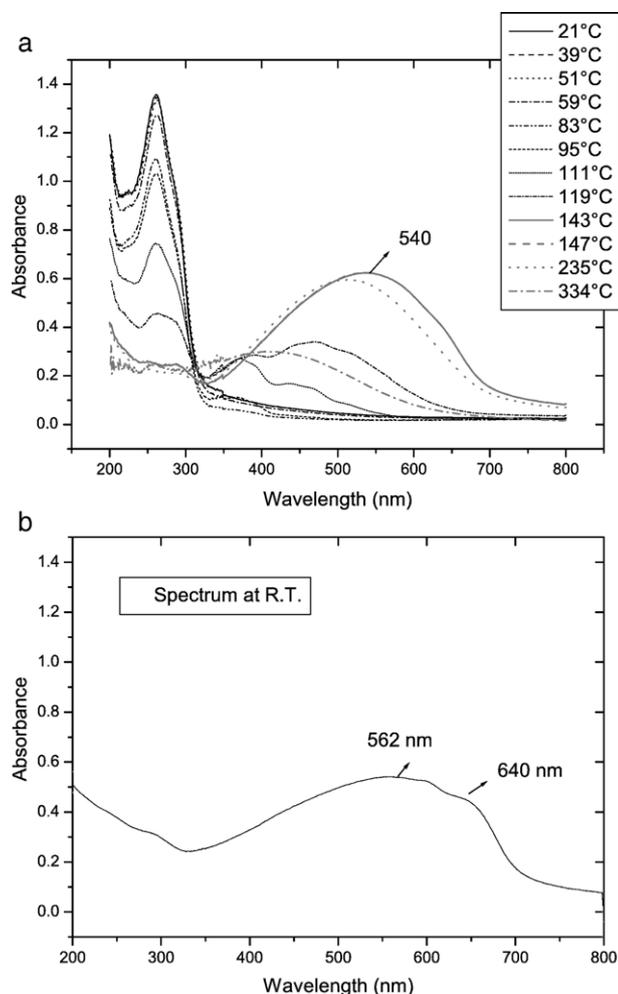
Fig. 1. *In situ* UV–Vis spectrum of **5a** at high temperature (a); UV–Vis spectrum at R.T. after conversion *in situ* of **5a**.

Table 2
Polymerisation results for **5a**, **8b** and **8c**

Polymer	Sample	# eq LDA	λ max (nm)	Mw (DMF)	PD (DMF)	Temperature (°C)	Yield (%)
5a	1	1.0	527	16.874	1.8	−78	45
	2	1.0	392	7.386	1.3	0	45
	3	1.0	425	8.681	1.4	R.T.	40
	4	1.2	546	10.761	1.4	−78	65
	5	1.5	527	13.096	1.3	−78	63
	6[a]	2.0	500	209.209	4	−78	50
				5.342[b]	1.2		
	7[a]	3.0	525	77.437	2.5	−78	60
				4.595[b]	1.1		
8b	8	1.0	535	14.224	1.1	−78	<5
	9	1.2	382	16.255	3.7	0	<5
	10	1.5	380	15.710	4.1	0	<5
8c	11	1.0	480	3.214	1.2	−78	<5
	12	1.2	Flat	6.895	2.7	0	<5
	13	1.5	537	17.228	1.4	0	<5

[a]Bimodal Mw distribution, [b]Low molecular weight peak.

140 °C through a decreased of the intensity of the typical dithiocarbamate groups absorption bands and, the appearance of a absorption peak at 930 cm^{-1} which is characteristic of the *trans*-vinylene double bonds as visualised in Fig. 4.

The cyclic voltamograms for a typical PTV polymer (Fig. 5) shows a reversible *p*- and *n*-doping behaviour. The electrochemical highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap (Eg) was calculated from the oxidation and reduction onset values. A band gap of 1.81 eV (HOMO=−5.1 eV LUMO=−3.3 eV) by cyclic voltammetry was found compared to a calculated optical band gap around 1.8–1.7 eV.

A thermogravimetric analysis (TGA) experiment on the precursor polymer with a molecular weight around 11.000 (sample 4, Table 2) was performed at a heating rate of 10 °C/min from room temperature up to 600 °C and with a continuous flow of nitrogen (50 mL/min). In Fig. 6, the weight loss of the
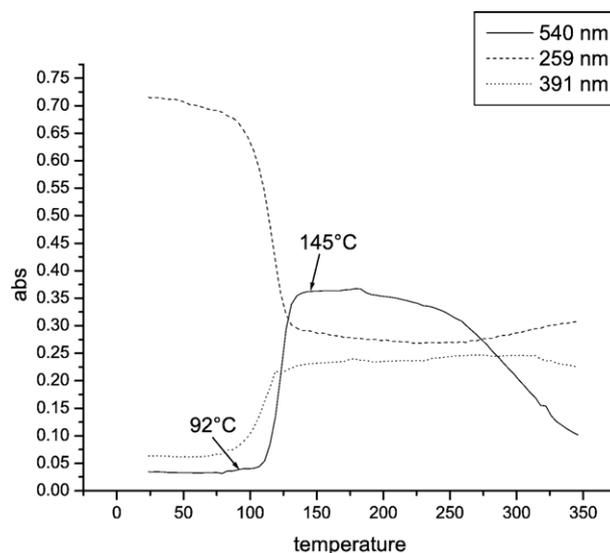
obtained, respectively 392 nm and 425 nm. This may be an indication of the presence of chemical defects and/or too low effective average conjugation length of the polymer backbone due to a too low molecular weight.

The λ$_{max}$ values mentioned above were all measured at high temperature during conversion and thus the thermochromic effect [27] is shifting the absorption spectrum to lower wavelength. In Fig. 2, the absorbance at λ$_{max}$ of both the dithiocarbamate precursor polymer and the conjugated polymer are plotted as a function of the temperature. From these profiles, it can be seen that the elimination of the dithiocarbamate groups of the thienyl precursor starts around 100 °C. In the region between 100° and 120 °C the formation and disappearance of oligomeric fragments with a λ$_{max}$ around 390 nm is visible (Fig. 1).

Also *in situ* FT-IR spectroscopy measurements were carried out. Fig. 3 shows a part of the FT-IR spectra of the precursor polymer during the conversion reaction obtained at different temperatures. This dithiocarbamate precursor polymer shows strong absorption bands at 1486, 1415, 1268 and 1206 cm^{-1} which all arise from the dithiocarbamate leaving group. By heating the precursor polymer at 2 °C/min from room temperature to 350 °C, the conversion reaction is observed between 85 and

Fig. 2. Absorbance profiles at 259, 391 and 540 nm of **5a** as a function of temperature.
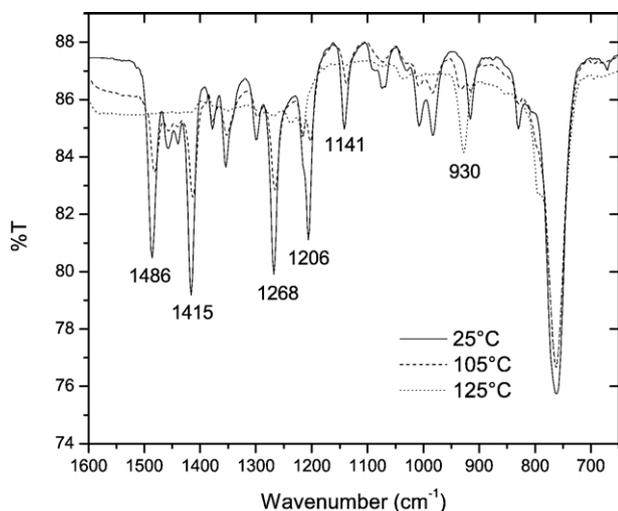
Fig. 3. IR spectra at different temperatures of **5a**.

Fig. 5. Voltamograms for a typical PTV polymer.

sample (solid lines) and the derivative of the weight loss (dashed lines) are plotted as a function of the temperature Two major steps of weight loss are visible: at 194 °C and 424 °C. The first step is related to the conversion step (evaporation of the elimination products coming from the thermal cleavage of the dithiocarbamathe groups). The second step of weight loss is assigned to a thermal degradation step (evaporation of the degradation products coming from a thermal degradation of the conjugated polymer backbone). The loss of weight below 100 °C is assigned to the evaporation of residual solvents: chloroform (bp=61 °C) and *n*-hexane (bp=69 °C).

The thermal stability of the same PTV dithiocarbamate precursor polymers (sample 4) was also evaluated by direct insertion probe pyrolysis mass spectrometry (DIP-MS) using a heating rate of 10 °C/min (Fig. 6). It shows two distinct signals at a maximum temperature of 200 and 400 °C. The first signal, based on the detected fragments $Et_2N(S)CS$, $Et_2N(S)C$ and NEt_2, can be assigned to the elimination of the dithiocarbamate groups and the

second one to the evaporation of the degradation products of the conjugated polymer. These observations are comparable with those obtained with TGA. The fact that a similar elimination temperature is observed in TGA (nitrogen atmosphere) and DIP-MS (vacuum) implies that the elimination products liberated are evaporated immediately at this temperature. Thus the elimination reaction and the evaporation process of the elimination products are not kinetically separated. The elimination temperature
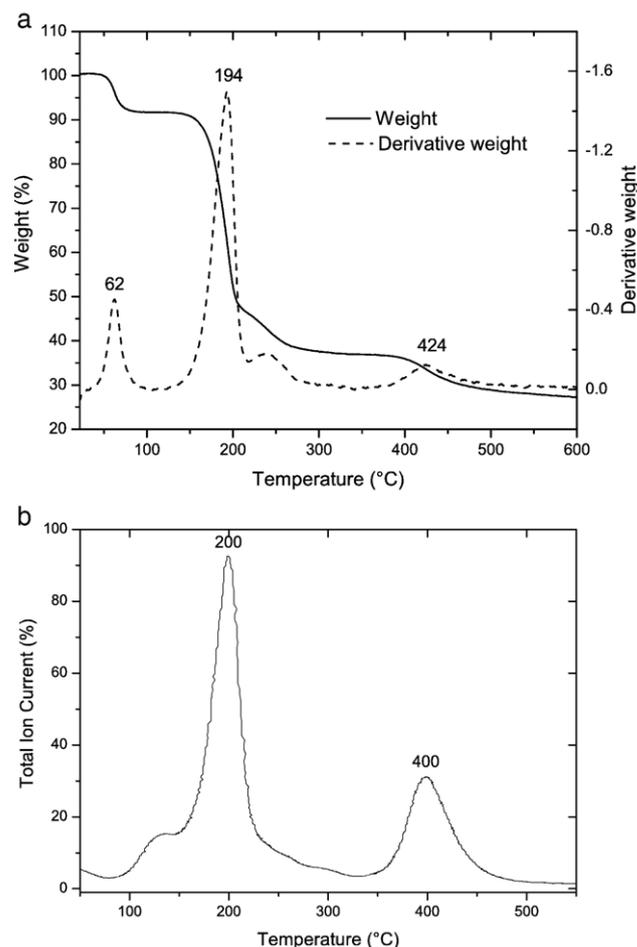

Fig. 4. IR absorption profiles at 1415, 1268 and 930 cm^{-1} of **5a** as a function of temperature.

Fig. 6. TGA thermogram and DIP-MS analysis of thienyl precursor polymer **5a** (sample 4).
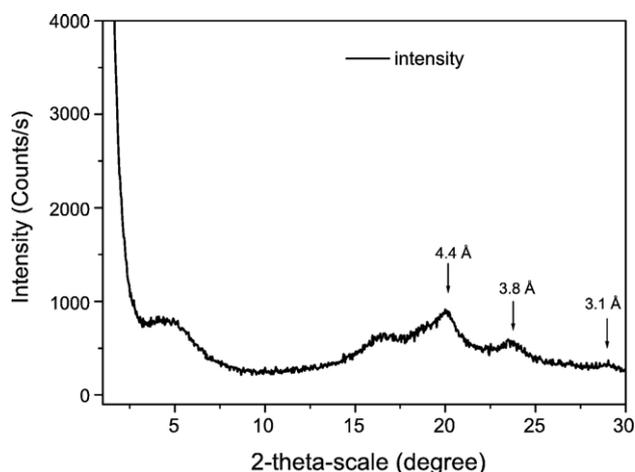
Fig. 7. X-Ray analysis for **5a** (sample 4).

Best devices	VOC [mV]	ISC [mA/cm^2]	FF	Efficiency [%]
L:PCBM 1:2 wt	350	3.5	0.49	0.61
H:PCBM 1:1 wt	350	4.85	0.45	0.76

observed with these techniques (200 °C) is higher than that obtained from *in situ* UV–Vis and *in situ* FT-IR (90–140 °C). This difference is attributed to the difference in heating rate (10 °C/min and 2 °C/min respectively).

DSC (Differential Scanning Calorimetry) measurements of precursor polymer with a molecular weight Mw around 11.000 (sample 4) were performed to determine the T_g (glass-transition
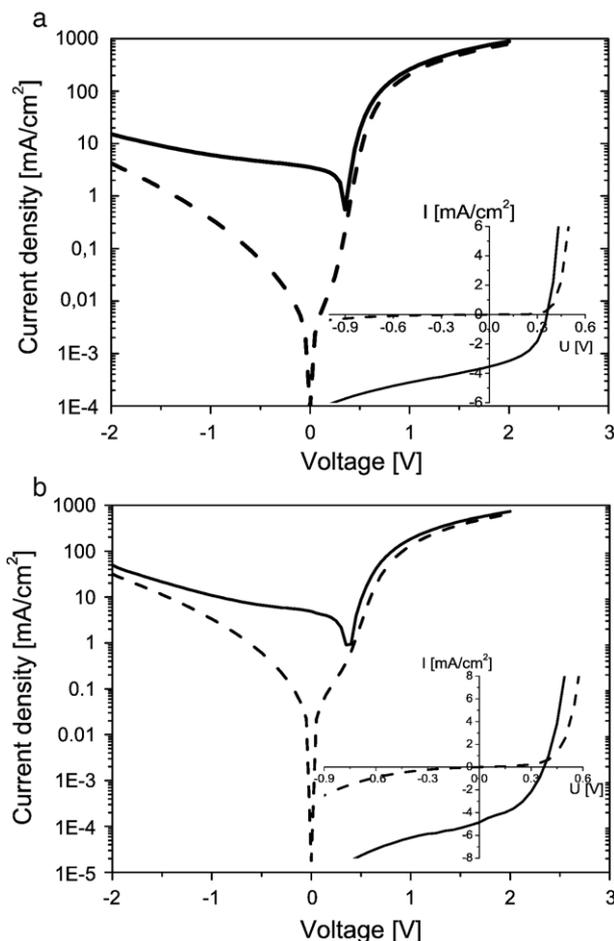
temperature) of the polymer. From the thermogram a T_g of around 69 °C is found. A comparable T_g is also found for precursor polymer with higher Mw ($T_g \cong 76$ °C). Since the elimination does not start before 92 °C (Fig. 2) we can conclude that the glass transition and the thermal conversion are two kinetically separated processes.

3.4. X-ray Diffraction spectroscopy (XRD)

The XRD profiles of PTV are given in Fig. 7. This conjugated polymer was obtained by conversion in solution of the precursor polymer (sample 4) in 1, 2-dichlorobenzene under reflux for 3 h. After precipitation of the solution in cold methanol, the conjugated polymer was filtered off and dried under vacuum in a desiccator. We could observe some minor ordering as indicated by the presence of weak peaks near $2\theta = 20°$, 23.5° and 29° in the XRD profile. This corresponds to distances of 4.4 Å, 3.8 Å and 3.1 Å respectively.

3.5. Mobility

For the precursor polymers (sample 5 and sample 6), the mobility was measured in an organic field effect transistor (OFET). A film from a 1% dichlorobenzene solution was obtained and subsequently converted to PTV by heating it from 25 °C to 155 °C at 2 °C/min. Then the sample was held at 155 °C for 20 min and than cooled down in argon atmosphere (cooling ramp −2 °C/min). The hole mobility was measured in OFET geometry, standard polymer dielectric substrates. The devices were measured in air without encapsulation. The curves are regular

Fig. 8. I–V characteristics (AM 1.5, 100 mW/cm^2) of the PTV: PCBM a) sample 5 and b) sample 6.
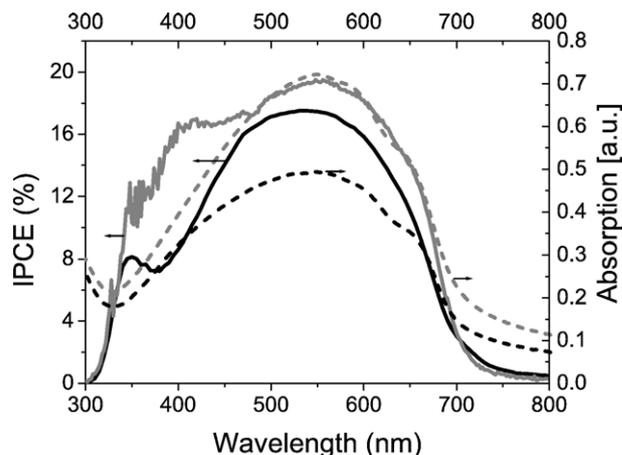

Fig. 9. IPCE % spectra of sample 5 (back solid line) and sample 6 (grey solid line) devices and the corresponding optical absorption for the pristine PTV (dashed lines).

and the resulting mobility are: $\mu_{fe} \sim 5 \times 10^{-5} \div 1 \times 10^{-4}$ cm^2/Vs (entry 5); $\mu_{fe} \sim 1 \times 10^{-3} \div 5 \times 10^{-3}$ cm^2/Vs (entry 6). The latter value is quite typical for PTV's obtained after conversion of a precursor [33].

3.6. Solar cell behaviour of PTV

PTV precursors with lowest (L sample 5) and highest (H sample 6) molecular weight were chosen for photovoltaic device testing. The best PV devices were obtained by preparing solutions of polymers L and H as donor component and the C$_{60}$-derivative 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6] C$_{61}$ (PCBM) as acceptor in the bulk heterojunction concept at the optimized weight ratio of 1:2 and 1:1 respectively in chlorobenzene at a concentration of 10 mg polymer/mL. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P, Bayer Germany) was spin-coated on top of indium-tin oxide (ITO) (Merck, Germany) coated glass (~ 25 W/sq) which had been cleaned in an ultrasonic bath with acetone and isopropyl alcohol. The active layer (precursor polymer: PCBM blend) was spin-coated on the PEDOT: PSS layer and then converted to PTV under inert atmosphere (argon) in a dry glove box at optimised conditions which were preliminary studied *via* UV–Vis measurements. Polymer L required 160 °C while polymer H needed a higher temperature of 190 °C for 10 min to obtain a sufficient conversion. 6 Å of lithium fluoride (LiF) and an 80 nm thick Al electrode was then deposited onto the blend film by thermal evaporation at $\sim 5 \times 10^{-6}$ mbar. All current–voltage (I–V) characteristics of the photovoltaic devices were measured using a Keithley SMU 2400 unit under inert atmosphere (argon) in a dry glove box. A Steuernagel solar simulator was used as the excitation source with a power of 100 mWcm^{-2} white light illumination (AM 1.5 conditions). A lock-in technique was used to measure the incident photon-to current efficiency (IPCE). With this technique the number of electrons produced from the cell under short-circuits conditions are related to the number of incident photons. Light intensity correction was performed using a calibrated Si photodiode.

I–V characteristics of ITO/PEDOT/PTV: PCBM/LiF/Al for the polymer L and H devices are shown in Fig. 8 both in dark and under AM 1.5 illumination. Table 3 compares the open-circuit voltage (VOC), short-circuit current (ISC), fill factor (FF) and conversion efficiency (h) for the different molecular weight PTVs. VOC and FF are comparable. The polymer with higher molecular weight (H) shows a significant enhanced photocurrent. This may be contributed to the higher molecular weight having higher mobility [34,35]. This because charge carriers can travel further along longer chains before they have to hop to another chain, and longer chains give charge carriers more opportunities for hoping to neighbouring chains. As a consequence photocurrent increases due to an enhancement of efficient charge transport.

Fig. 9 reports the spectrally resolved photocurrent (IPCE) of the polymer L (black line) and polymer H (grey line) devices together with the corresponding absorption spectra of the pristine PTV (dashed lines). The IPCE spectrum of both devices shows an onset of the photocurrent at about 750 nm (1.65 eV) close to the optical band gap and exhibits a maximum of 17%

and 20% at 550 nm for entries 5 and 6. The IPCE increases $\sim 3\%$ for the highest molecular weight PTV.

In comparison to other low band gap polymer/PCBM systems such as polyfluorene/PCBM [36] and poly[5,7-bis-(3-octylthiophene-2-yl)thieno{3,4-b}pyrazine]/PCBM [37] the short-circuit currents achieved in this study with the PTV/PCBM blend is significantly higher, up to about 5 mA/cm^2, leading to the final power efficiency of 0.76%. Similar results were obtained recently for the low band gap material poly(di-2-thienylthienopyrazine) [38].

The low band gap polymer PTV can lead to a better matching of the absorption spectrum of the donor material to the solar emission spectrum. However, high performance devices require significant higher external quantum efficiencies. Molecular weight seems to have an effect on the performance of bulk heterojunction solar cells.

4. Conclusions

The dithiocarbamate precursor route, was used for the synthesis of a precursor polymer toward Poly(2,5-Thienylene Vinylene) (PTV). Synthesis of the corresponding thiophene bismethylene *N,N*-diethyl dithiocarbamate monomer was easily achieved. The polymerisation involved a reaction with different concentrations of base (LDA) in dry THF. The polymerisation step was optimized and the best conditions were found at a temperature of −78 °C using 2 eq. of base. The use of the dithiocarbamate precursor route for the synthesis of PTV, as a precursor route, shows some distinct advantages compared to the xanthate precursor route such as: (i) yielding higher molecular weight; (ii) lower values of polydispersities; (iii) a higher value for λ_{max} of the conjugated PTV polymers and therefore higher effective conjugation lengths; (iv) a promising value for the field effect mobility and the energy conversion efficiency in organic solar cells. To appreciate the latter, one should take in account that the active layer is produced by converting a blend of a precursor together with PCBM at relative high temperature. All these observations indicate that the dithiocarbamate precursor route may provide a solution for the problem associated with the synthesis of electron rich Poly (*p*-Arylene Vinylene)s precursor routes.

Acknowledgments

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