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Poly(*p*-phenylene vinylene) derivatives with ester- and carboxy-functionalized substituents: a versatile platform towards polar functionalized conjugated polymers

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Abstract

A polar functionalized poly(*p*-phenylene vinylene) (PPV) derivative, ester containing poly(1,4-(2-(pentyloxy-5-carboxy methylester)-5-methoxyphenylene)vinylene), has been prepared via the sulfinyl precursor route. Subsequently, the carboxylic acid containing poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene) is readily obtained by the basic hydrolysis of the ester side groups. This carboxylic acid substituted polymer exhibits significantly improved optical properties as compared to previously reported similar polymers. To obtain polar functionalized PPV derivatives with more complex tailored substituents a versatile novel approach is presented based on the Mitsunobu reaction conditions via a post-polymerization functionalization of the carboxylic acid side groups. Using these reaction conditions substituents containing various ester groups, i.e. 4-nitrobenzyl, 2-nitrobenzyl, 5-(methyl)furfural and 3-*N*,*N*-dimethylamino-1-propane, have been covalently attached to the phenylene ring. Analytical data of the functionalized polymers are consistent with a quantitative functional group substitution. The results demonstrate that the employed functionalization method allows for the introduction of a large variety of polar substituents in a straightforward manner.

Keywords: Polar functionalized PPV; Sulfinyl precursor route; Mitsunobu reaction

1. Introduction

Currently, functional polymers attract considerable attention due to their significantly expanded property and application range as compared to their nonfunctional counterparts. Hence, it can be expected that functional polymers will increasingly penetrate into industrially feasible and economically viable large scale technology. So far, this penetration of functional polymers has been hampered by the relative complexity and cost of their preparation, which is often difficult due to chemical and/or phase incompatibilities or antagonisms [1]. In this article a versatile new approach is presented to obtain several polar functionalized poly(*p*-phenylene vinylene) (PPV) derivatives in a straightforward manner.

The discovery of luminescence in PPV [2], sparked substantial interest in this polymer and its derivatives for applications, such as light emitting diodes, field effect transistors [3], sensors [4] and photovoltaic cells [5]. A variety of common synthetic procedures to obtain PPV-type polymers, are based on precursor methods, in which a soluble precursor polymer is converted to the conjugated structure in situ or in an additional conversion step [6–9]. The use of such precursor routes is an excellent method to introduce sufficient processability. This processability is essential for the successful incorporation of the conjugated polymer into a variety of devices. Although in some cases, processability can be achieved by the introduction of solubilizing side chains, unfortunately this is not always possible, especially not for applications such as biosensors in which complex functionalized materials are required. The most frequently employed synthetic route is the Gilch route [7,10]. In this route, the monomer consists of a

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symmetrically substituted bis chloro *p*-xylene derivative. However, over the last years, a new and promising precursor route towards PPV-type polymers was developed in our laboratory, the so-called sulfinyl route, which can be distinguished from other precursor routes by the asymmetrically substituted monomers [9,11]. Previous studies have indicated a notable improvement of the properties of polymers prepared via the sulfinyl route as compared to the Gilch route [12], such as the achievement of lower defect levels [13] and an enhancement in the power conversion efficiency for bulk heterojunction solar cells [14]. The improved properties of PPV-type polymers obtained via the sulfinyl route can be attributed to the higher chemical selectivity during polymerization. Within this context the sulfinyl route was the route of choice to obtain the polar functionalized PPV derivatives. It is demonstrated that indeed improved optical properties are obtained as compared to previously reported similar polymers.

Currently much interest exists in polar functionalized PPV derivatives [15]. They exhibit promising properties for a variety of applications in which the polar side groups of the conjugated polymers can introduce additional order. Examples include conjugated polymer electrolytes [16], self-assembled multilayers [17,18], as well as organized hybrid systems [19]. Various synthetic options for the polymerization of polar functionalized conjugated polymers have been extensively reviewed by others [15]. Generally, functionalized PPV derivatives have been obtained by incorporating the desired side chain into the reactive monomer, which is subsequently polymerized. This strategy has been successfully employed for a limited number of polar substituents. However, functional group incompatibility with the polymerization reaction can result in insufficiently high molecular weights or may even hamper polymerization altogether. To avoid the limitations of direct polymerization, a synthetic strategy that allows a post-polymerization functionalization of the PPV with polar moieties is of considerable interest. Thus far, most reported post-polymerization functionalization reactions have been limited to the deprotection of functional groups after polymerization [17,19], a method which only allows for the introduction of a limited number of functionalities.

This article describes a versatile novel approach which allows the incorporation of a sheer unlimited number of polar molecules as substituents. To this end a carboxylic acid containing PPV derivative, poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene) **8**, has been prepared. To avoid solubility problems, the corresponding methylester is used during the synthesis of the monomer and precursor polymer. After formation of the ester substituted PPV derivative, these ester side groups have been hydrolyzed quantitatively giving **8**. The carboxylic acid groups of **8** readily react with alcohol functionalized molecules under the mild, neutral conditions of the Mitsunobu reaction to afford the corresponding carboxylic esters. Using this method four novel polar functionalized PPV derivatives with substituents containing various ester groups, i.e. 4-nitrobenzyl, 2-nitrobenzyl, 5-(methyl)furfural and 3-*N*,*N*-dimethylamino-1-propane, have been prepared.

2. Experimental section

2.1. General

NMR spectra were recorded with a Varian Inova Spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR. Analytical size exclusion chromatography (SEC) was performed using a spectra series P100 (Spectra Physics) pump equipped with a pre-column (5 μm, 50×7.5 mm, guard, Polymer Labs) and two mixed-B columns (10 μm, 2×300×7.5 mm, Polymer Labs) and a Refractive Index (RI) detector (Shodex) at 40 °C. Either THF or DMF was used as the eluent at a flow rate of 1.0 ml/min. Molecular weight distributions are given relative to polystyrene standards. GC-MS data were obtained with a Varian TSQ 3400 Gas Chromatograph and a TSQ 700 Finnigan Mat mass spectrometer. Glass transition temperatures (T_g) were determined through differential scanning calorimetry (DSC) on a DSC 910-2000 analyzer. The samples (10 mg) were heated from −100 to 150 °C at a heating rate of 10 °C/min under N_2 atmosphere. The second heating curves were evaluated. UV–vis measurements were performed on a Cary 500 UV–vis-NIR spectrophotometer (scan rate 600 nm/min, continuous run from 200 to 800 nm). FT-IR spectra were collected with a Perkin–Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). Fluorescence spectra were obtained with a Perkin–Elmer LS-5B luminescence spectrometer. In situ elimination reactions were performed in a variable temperature oven (Harrick). This oven can be positioned in the beam of either the FT-IR spectrometer or the UV–vis-NIR-spectrophotometer. Elemental analysis was performed with a Flash EA 1112 Series CHNS-O analyzer. All chemicals were purchased from Aldrich or Acros and used without further purification unless otherwise stated. Tetrahydrofuran (THF) and dioxane were distilled from sodium/benzophenone.

2.2. Monomer synthesis

2.2.1. 6-(4-Methoxy-phenoxy)-hexanoic acid ethyl ester (*1*)

A mixture of 4-methoxyphenol (15.0 g, 120 mmol), NaO*t*Bu (13.9 g, 145 mmol) and EtOH (125 ml) was stirred for 1 h at room temperature under N_2 atmosphere, after which ethyl 6-bromohexanoate (32.1 g, 145 mmol) and sodium iodide (0.5 g, 3.3 mmol) were added. The resulting solution was stirred for 4 h at reflux temperature. The reaction was quenched with water (125 ml), and then extracted with CH_2Cl_2 (3×50 ml). The combined organic extracts were dried over anhydrous $MgSO_4$. Evaporation of

the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography (SiO_2, eluent CH_2Cl_2) as a colorless oil (29.3 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.74 + 6.76$ (dd, 4H), 3.97 (t, 2H), 3.72 (t, 2H), 3.65 (t + s, 5H), 3.54 (t, 2H), 3.23 (s, 1H). Mass (GC-MS, EI): 266 $[M+1]^+$, 221 $[M+1]^+ - C_2H_5O$.

2.2.2. 6-(2,5-Bis-chloromethyl-4-methoxy-phenoxy)-hexanoic acid (*2*)

To a stirred mixture of **1** (7.2 g, 27 mmol) and paraformaldehyde (2.23 g, 74 mmol), concentrated HCl (13 ml) was added dropwise under N_2 atmosphere. Subsequently, acetic anhydride (26 ml, 0.28 mol) was added at such a rate that the temperature did not exceed 70 °C. After the addition was complete, the resulting solution was stirred at 60 °C for 3 h after which it was cooled down to room temperature and poured into water (100 ml). The resulting precipitate was filtered off, redissolved in CH_2Cl_2 (100 ml) and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the carboxylic acid as a white solid (9.16 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.89 + 6.88$ (2s, 2H), $4.61 + 4.60$ (2s, 4H), 3.97 (t, 2H), 3.83 (s, 3H), 3.39 (t, 2H), 1.81 (m, 2H), 1.72 (m, 2H), 1.58 (m, 2H).

2.2.3. Bis-tetrahydrothiophenium salt of 6-(2,5-bis-chloromethyl-4-methoxy-phenoxy)-hexanoic acid methyl ester (*3*)

To a solution of **2** (3.0 g, 9 mmol) in MeOH (30 ml), tetrahydrothiophene (3 ml, 36 mmol) was added. The mixture was allowed to react for 14 h at 50 °C, after which the total volume was reduced to 15 ml by evaporation at room temperature. Subsequently, the product was precipitated in cold acetone (150 ml) after which the bissulfonium salt was filtered off as a white solid (3.25 g, 69% yield). ^{1}H NMR (300 MHz, D_2O): $\delta = 7.12 + 7.11$ (2s, 2H), $4.44 + 4.43$ (2s, 4H), 4.03 (t, 2H), 3.81 (s, 3H), 3.58 (s, 3H), 3.40 (m, 8H), 2.34 (t, 2H), 2.24 (m, 8H), 1.75 (m, 2H), 1.59 (m, 2H), 1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 177.5$, 151.9, 151.3, 119.7, 119.6, 116.2, 115.4, 69.1, 56.2, 52.1, 43.0, 41.5, 33.5, 28.3, 28.0, 24.9, 23.9. FT-IR (NaCl, cm^{-1}): 3000, 2943, 2877, 1734 (ν_{C-O}), 1513, 1465, 1447, 1400, 1314, 1230, 1165, 1103, 1035, 910.

2.2.4. 6-(5-Chloromethyl-4-methoxy-2-octylsulfanylmethyl-phenoxy)-hexanoic acid methyl ester (*4*)

A mixture of *n*-octane thiol (1.0 g, 7 mmol) and NaO*t*Bu (0.67 g, 7 mmol) in MeOH (40 ml) was stirred for 30 min at room temperature after which a clear solution was obtained. This solution was added dropwise to a solution of **3** (3.8 g, 7 mmol) in MeOH (130 ml). The reaction mixture was stirred for 2 h after which it was concentrated under reduced pressure. Subsequently, *n*-octane (100 ml) was added and evaporated again to remove the tetrahydrothiophene. This sequence was repeated three times. After removal of the solvents under reduced pressure, the residue was redissolved in CH_2Cl_2 (100 ml) and the organic layer was extracted with water (3×100 ml). The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography (SiO_2, eluent CH_2Cl_2) as a yellow viscous oil (1/1 mixture of regio-isomers; 2.8 g, 88% yield). ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 6.90 + 6.88 + 6.84 + 6.82$ (4s, 2H), $4.61 + 4.60$ (2s, 2H), 3.94 (m, 2H), $3.83 + 3.81$ (2s, 3H), $3.79 + 3.78$ (2s, 3H), $3.69 + 3.68$ (2s, 2H), 3.65 (s, 3H), 2.44 (t, 2H), 2.33 (t, 2H), 1.79 (m, 2H), 1.71 (m, 2H), 1.52 (m, 2H), $1.30 - 1.23$ (m, 12H), 0.85 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.1$, 151.1, 150.5, 128.7, 124.7, 114.3, 113.3, 68.6, 56.2, 51.5, 39.2, 34.0, 31.9, 31.8, 30.2, 29.2, 29.0, 28.5, 25.7, 24.6, 22.6, 14.1. Mass (GC-MS, EI): 458 $[M+1]^+$, 423 $[M+1]^+ - HCl$, 329 $[M+1]^+ - C_7H_{13}O_2$, 313 $[M+1]^+ - C_8H_{17}S$, 277 $[M+1]^+ - C_8H_{17}S–HCl$, 185 $[M+1]^+ - C_8H_{17}S–C_7H_{13}O_2$, 129 $C_7H_{13}O_2$.

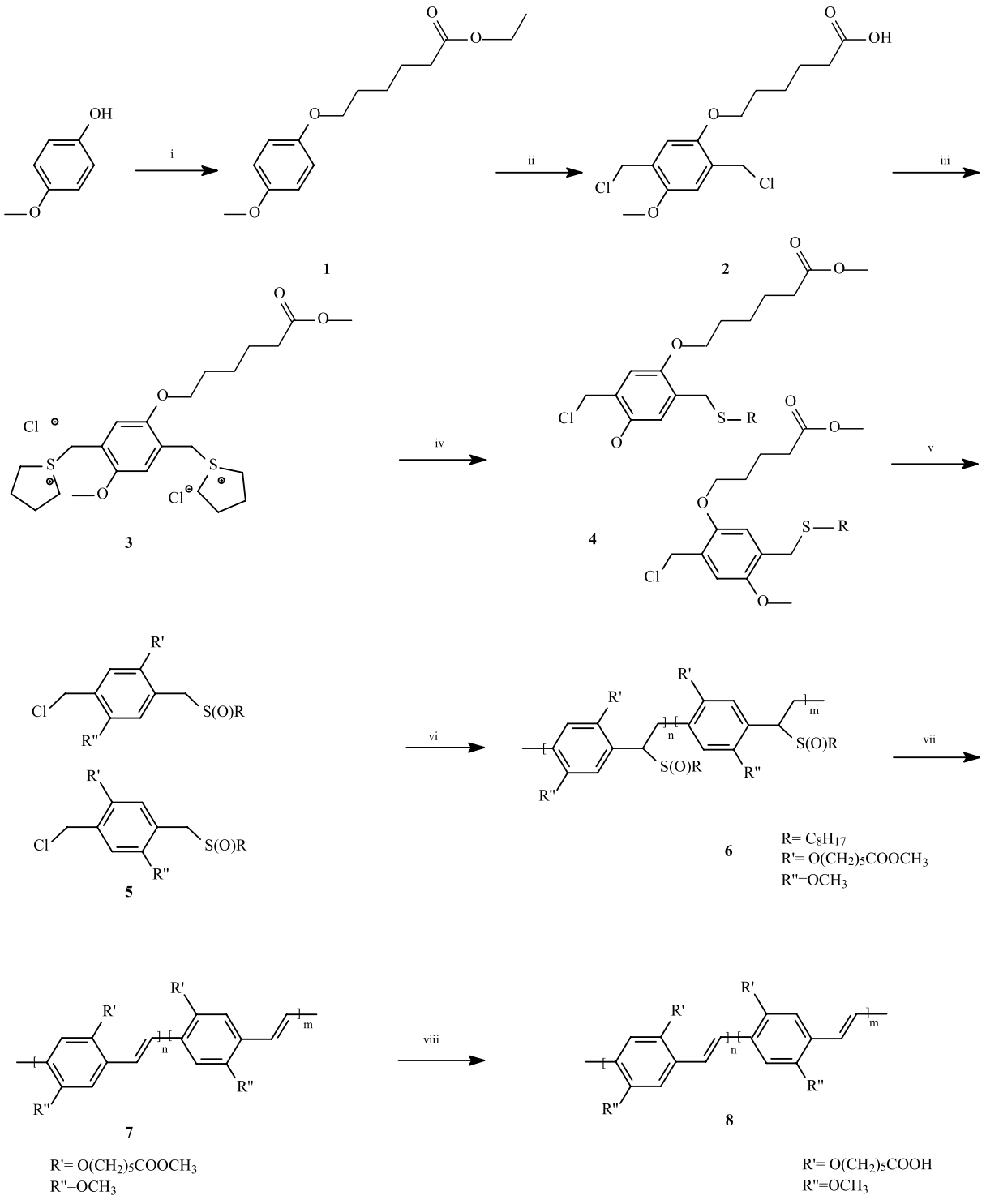
2.2.5. 6-(5-Chloromethyl-4-methoxy-2-octylsulfinylmethyl-phenoxy)-hexanoic acid methyl ester (*5*)

An aqueous (35 wt%) solution of H_2O_2 (1.2 g, 12.4 mmol) was added dropwise to a mixture of **4** (2.8 g, 6 mmol), concentrated HCl (0.05 ml) and TeO_2 (0.06 g, 0.36 mmol) in dioxane (50 ml). As soon as **4** was consumed (TLC), 100 ml of brine was added to quench the reaction. The reaction mixture was extracted with $CHCl_3$ (3×50 ml) after which the combined organic extracts were dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography (SiO_2, eluent CH_2Cl_2/MeOH 19/1) as an orange viscous oil (1/1 mixture of regio-isomers; 2.6 g, 93% yield). Anal. Calcd For $C_{24}H_{39}ClO_5S$: C 60.67, H 8.27, O 16.83, S 6.75. Found C 59.84, H 8.32, O 17.23, S 5.08; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.88 + 6.86 + 6.85 + 6.84$ (4s, 2H), $4.56 + 4.55$ (2s, 2H), $4.13 + 4.11 + 4.20 + 4.00$ (2dd, 2H, $^3J = 12.6$ Hz), 3.91 (m, 2H), $3.77 + 3.75$ (2s, 3H), 3.60 (s, 3H), 2.67 (m, 2H), 2.29 (t, 2H), $1.78 - 1.61$ (m, 6H), $1.49 - 1.18$ (m, 11H), 0.81 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.7$, 173.6, 151.0, 150.7, 150.5, 150.2, 126.4, 126.2, 119.7, 119.6, 115.5, 114.5, 113.6, 112.7, 68.4, 68.2, 55.9, 55.8, 52.7, 52.3, 51.3, 51.2, 41.1, 41.0, 33.7, 33.6, 31.5, 30.6, 28.9, 28.7, 28.6, 28.5, 25.4, 25.3, 24.4, 22.3, 13.8. FT-IR (NaCl, cm^{-1}): 2928 (ν_{C-H} aliph), 1738 (ν_{C-O}), 1045 (ν_{C-S}) (Scheme 1).

2.3. Polymer synthesis

2.3.1. Precursor polymer of 6-(5-chloromethyl-4-methoxy-2-octylsulfinylmethyl-phenoxy)-hexanoic acid methyl ester (*6*)

To a solution of monomer **5** (2.0 g, 4.21 mmol) in 2-BuOH (30 ml), a solution of Na*t*BuO (0.53 g, 5.47 mmol) in 2-BuOH (12 ml) was added in one portion using a thermostatic flask and funnel (30 °C) after both solutions



Scheme 1. Synthesis of the sulfinyl monomer and polymers **1–8** (i) Na*t*BuO, ethyl 6-bromohexanoate, NaI_{cat}, EtOH(reflux); (ii) *p*-CH_2O, Ac_2O, HCl, 60 °C; (iii) THT, MeOH, 50 °C; (iv) RSH, Na*t*BuO, MeOH; (v) H_2O_2, TeO_2, HCl_{cat}, 1,4-dioxane; (vi) Na*t*BuO, 2-BuOH; (vii) toluene (reflux); (viii) *t*BuO, 1,4-dioxane.

were purged with N_2. The polymerization was allowed to proceed for 1 h at 30 °C after which it was quenched by pouring the reaction mixture in a well stirred amount of ice water (200 ml). After extraction with CH_2Cl_2 (3×200 ml), the combined organic layers were evaporated under reduced pressure giving the crude product, which was used without further purification (1.18 g, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.0-6.3$ (2H), 4.5 (2H), 4.1−3.6 (6H), 3.4 (3H), 2.4−1.8 (4H), 1.8−1.2 (18H), 0.9 (3H). FT-IR (NaCl, cm^{-1}): 2929, 2856, 1728 (ν_{C-O}), 1506, 1463,

1409, 1212, 1032. SEC (THF) $M_w = 2.51 \times 10^5$ g/mol ($D = M_w/M_n = 2.1$). DSC $T_g = -39$ °C.

2.3.2. Poly(1,4-(2-(pentyloxy-5-carboxy methylester)-5-methoxyphenylene)vinylene) (7)

The conjugated polymer **7** was prepared via two methods, i.e. thermal conversion in a thin film (**7a**) and thermal conversion in solution (**7b**). However, for all further chemical conversions only **7b** was used.

To prepare **7a**, precursor polymer **6** was spincoated from a $CHCl_3$ solution (6 mg/ml) on a KBr (diameter 25 mm, thickness 1 mm) or quartz (diameter 25 mm, thickness 3 mm) substrate at 500–700 rpm. Subsequently, the spin-coated substrate was placed in an oven and heated at 2 °C/min up to 300 °C under a continuous flow of N_2 during which the samples were in direct contact with the heating element.

To prepare **7b**, a stirred solution of **6** (2.19 g, 4.99 mmol) in toluene (125 ml) was purged with N_2 for 1 h, after which the elimination reaction was allowed to proceed at 110 °C for 3 h. Subsequently, the total volume was reduced to 50 ml by evaporation and the resulting orange red solution was precipitated dropwise in cold EtOH (1250 ml). The resulting polymer was filtered off, washed with EtOH and redissolved in toluene (125 ml). The elimination procedure was repeated after which crude **7b** was filtered off again and dried at room temperature under reduced pressure. For purification, the crude **7b** was dissolved in boiling THF (25 ml) and after cooling to 40 °C dropwise precipitated in EtOH (250 ml), giving **7b** as a red, fibrous polymer (1.02 g, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.5-7.3$ (2H), 7.2−6.9 (2H), 4.2 (2H), 3.8 (3H), 3.6 (3H), 2.3 (2H), 1.8−1.3 (6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.1$, 151.3, 150.8, 127.2, 123.2, 110.4, 109.1, 69.0, 56.1, 49.5, 33.8, 28.6, 25.5, 24.7. FT-IR (NaCl, cm^{-1}): 2934, 2866, 1728 (ν_{C-O}), 1505, 1463, 1413, 1205, 1034, 969. SEC (THF) $M_w = 2.90 \times 10^5$ g/mol ($D = M_w/M_n = 2.0$). UV–vis $\lambda_{max} =$ 479 nm (THF), $\lambda_{max} = 459$ nm ($CHCl_3$). Photoluminescence emission maximum 546 nm ($\lambda_{ex} = 459$ nm, $CHCl_3$). DSC $T_g = 55$ °C.

2.3.3. Poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene) (8)

A solution of polymer **7b** (200 mg, 0.72 mmol repeating units) and dioxane (40 ml) was heated to reflux temperature after which a solution of K*t*BuO (0.87 g, 7.6 mmol) in water (1 ml) was added. After 4 h stirring at reflux temperature the reaction mixture was added dropwise to a well stirred amount of ice water (400 ml), neutralized with aqueous HCl (1 M) and the resulting precipitate was filtered off and washed with water (3×50 ml). The polymer was dried at room temperature under reduced pressure giving **8** as a red fibrous polymer (0.149 g, 79% yield). Anal. Calcd For $C_{15}H_{18}O_4$: C 68.69, H 6.92, O 24.40. Found C 68.83, H 7.33, O 23.55; ^{1}H NMR (300 MHz, DMSO): $\delta = 7.7-7.5$ (4H), 7.2 (1H), 4.2−3.7 (5H), 2.2 (2H), 2.0−1.2 (6H); ^{13}C NMR (75 MHz, DMSO): $\delta = 174.5$, 151.2, 150.7, 126.3, 124.4, 110.8, 109.9, 68.6, 56.0, 33.7, 28.8, 25.3, 24.4. FT-IR (NaCl, cm^{-1}): 2952, 2869, 2700 (broad, ν_{O-H}), 1709 (ν_{C-O}), 1503, 1464, 1412, 1207, 1036, 972. SEC (DMF) $M_w = 2.23 \times 10^5$ g/mol ($D = M_w/M_n = 2.5$). UV–vis $\lambda_{max} =$ 490 nm (DMSO), $\lambda_{max} = 470$ nm ($CHCl_3$). Photoluminescence emission maximum 540 nm ($\lambda_{ex} = 470$ nm, $CHCl_3$). DSC $T_g = 51$ °C (Scheme 1).

2.4. Post-polymerization functionalization

2.4.1. 5-(Methyl)furfural ester of 8 (A)

A solution of polymer **8** (100 mg, 0.38 mmol repeating units) in dry THF (10 ml) was cooled to 0 °C under N_2 atmosphere. To this solution an alcohol functionalized molecule, i.e. 5-(hydroxymethyl)furfural (0.048 g, 0.38 mmol) and triphenylphosphine (120 mg, 0.46 mmol) were added and the mixture was stirred for 10 min. Subsequently, diethyl azodicarboxylate (0.2 ml, 0.46 mmol) was slowly added via a syringe. The mixture was allowed to warm to room temperature over a period of 2 h and stirred at room temperature for an additional 24 h after which the reaction mixture was added dropwise to a non-solvent, i.e. *n*-hexane (100 ml) whereupon the polymer precipitated. After filtration and drying under vacuum polymer **A** was obtained as a red solid (42 mg, 30% yield). ^{1}H NMR (300 MHz, DMSO): $\delta = 9.6$ (1H), 7.5−6.5 (6H), 5.1 (2H), 4.2−3.7 (5H), 2.2 (2H), 1.9−1.2 (6H). FT-IR (NaCl, cm^{-1}): 2983, 2871, 1724 (ν_{C-O}), 1680, 1522, 1484, 1438, 1410, 1380, 1342, 1207, 1120, 1064, 723. SEC (DMF) $M_w = 1.29 \times 10^4$ g/mol ($D = M_w/M_n = 2.6$). UV–vis $\lambda_{max} = 469$ nm (THF), $\lambda_{max} = 438$ nm ($CHCl_3$). Photoluminescence emission maximum 530 nm ($\lambda_{ex} = 438$ nm, $CHCl_3$).

2.4.2. 2-Nitrobenzyl ester of 8 (B)

Polymer **B** was prepared following the procedure described for polymer **A** using 2-nitrobenzylalcohol (0.058 g, 0.38 mmol) as the alcohol functionalized molecule in the reaction and methanol (100 ml) as the non-solvent in the precipitation. After filtration and drying under vacuum polymer **B** was obtained as a red solid (67 mg, 43% yield). ^{1}H NMR (300 MHz, DMSO): $\delta = 8.1$ (2H), 7.8−7.3 (4H), 7.2 (2H), 5.4 (2H), 4.1−3.9 (5H), 2.3 (2H), 1.9−1.2 (6H). FT-IR (NaCl, cm^{-1}): 2932, 2867, 1739 (ν_{C-O}), 1613, 1528 (ν_{NO_2}), 1504, 1464, 1411, 1343 (ν_{NO_2}), 1208, 1035, 790, 727. SEC (DMF) $M_w = 5.09 \times 10^4$ g/mol ($D = M_w/M_n = 2.7$). UV–vis $\lambda_{max} = 488$ nm (THF), $\lambda_{max} = 437$ nm ($CHCl_3$). Photoluminescence emission maximum 536 nm ($\lambda_{ex} =$ 437 nm, $CHCl_3$).

2.4.3. 4-Nitrobenzyl ester of 8 (C)

Polymer **C** was prepared following the procedure described for polymer **A** using 4-nitrobenzylalcohol (0.058 g, 0.38 mmol) as the alcohol functionalized molecule in the reaction and methanol (100 ml) as the non-solvent in

the precipitation. After filtration and drying under vacuum polymer **C** was obtained as a red solid (86 mg, 55% yield). ^{1}H NMR (300 MHz, DMSO): $\delta = 8.1$ (2H), 7.6−7.3 (4H), 7.2−7.1 (2H), 5.2 (2H), 4.2−3.8 (5H), 2.4 (2H), 1.9−1.2 (6H). FT-IR (NaCl, cm^{-1}): 2939, 2867, 1737 (ν_{C-O}), 1606, 1520 (ν_{NO_2}), 1504, 1438, 1410, 1341 (ν_{NO_2}), 1206, 1157, 1119, 1030, 859, 722. SEC (DMF) $M_w = 1.82 \times 10^4$ g/mol ($D = M_w/M_n = 2.4$). UV–vis $\lambda_{max} = 486$ nm (THF), $\lambda_{max} = 431$ nm ($CHCl_3$). Photoluminescence emission maximum 533 nm ($\lambda_{ex} = 431$ nm, $CHCl_3$).

*2.4.4. 3-N,N-Dimethylamino-1-propane ester of **8** (**D**)*

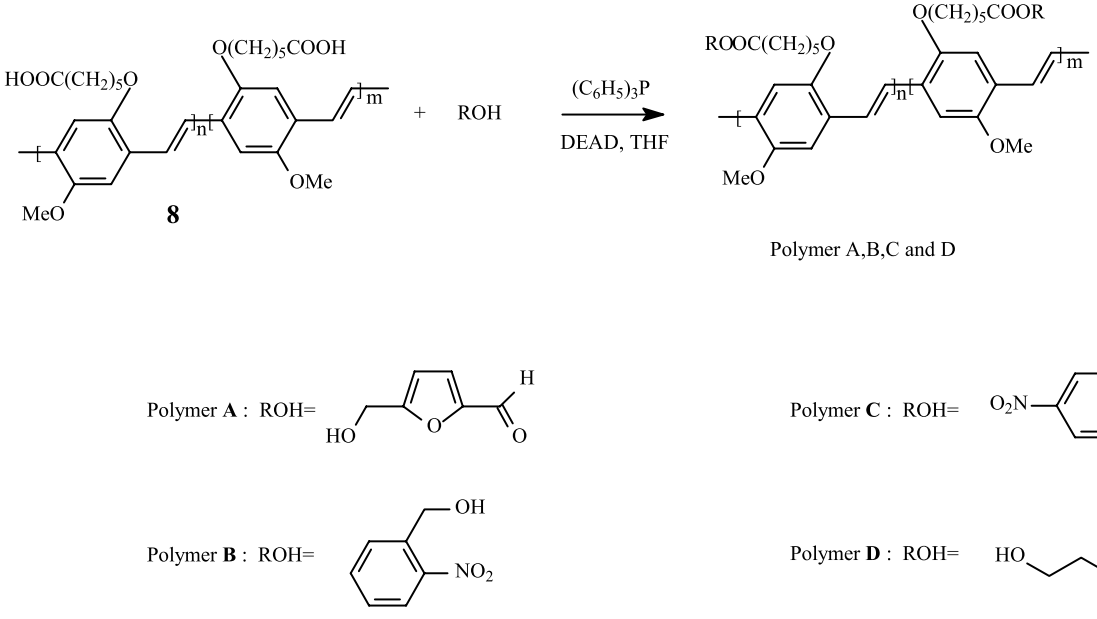
Polymer **D** was prepared following the procedure described for polymer **A** using 3-*N*,*N*-dimethylamino-1-propanol (0.039 g, 0.38 mmol) as the alcohol functionalized molecule in the reaction and *n*-hexane (100 ml) as the non-solvent in the precipitation. After filtration and drying under vacuum polymer **D** was obtained as a red solid (54 mg, 38% yield). Polymer **D** is insoluble in common organic solvents. FT-IR (NaCl, cm^{-1}): 2937, 2864, 1730 (ν_{C-O}), 1501, 1462, 1406, 1389, 1206, 1033 (Scheme 2).

3. Results and discussion

3.1. Monomer and polymer synthesis

In view of the higher chemical selectivity during polymerization, the sulfinyl route was chosen as the precursor method of choice to obtain the functionalized PPV derivatives (vide supra). The monomer, 6-(5-chloromethyl-4-methoxy-2-octylsulfinylmethyl-phenoxy)-hexanoic acid methyl ester **5**, was prepared in a five step reaction according to Scheme 1. Starting from 4-methoxyphenol and ethyl 6-bromohexanoate, a Williamson etherification gives **1**. Subsequently, **1** is chloromethylated using concentrated HCl and formaldehyde in acetic anhydride to give **2**, according to a literature procedure [15,20]. The next step involves the formation of the bissulfonium salt **3**. This procedure is well documented in literature for comparable systems [21]. The crucial step in the monomer synthesis is the introduction of a thioether group by reaction of the symmetrical bissulfonium salt **3** with an equimolar amount of an alkylthiolate anion. Azeotropic removal of tetrahydrothiophene affords the mono-substituted thioether **4**, which can be selectively oxidized to the desired sulfinyl monomer **5**, using mild oxidation conditions. It should be noted that both **4** and **5** are present in a 1/1 mixture of regio-isomers, which is used without further separation.

The polymerization reaction of sulfinyl monomers giving precursor polymer **6** proceeds via a *p*-xylylene intermediate, i.e. a *p*-quinodimethane system, which acts as the actual monomer. In order to demonstrate that the polymerization using the sulfinyl precursor route of monomer **5** with side groups containing a polar ester is straightforward and comparable to the polymerization of similar monomers with apolar alkyl substituents [22,23], the formation of the *p*-quinodimethane system was followed with in situ UV–vis spectroscopy. When monomer and base solutions are mixed in the measuring cell, within seconds a new absorption band at $\lambda_{max} = 320$ nm appears that originates from the *p*-quinodimethane system (Fig. 1). The measurements demonstrate that the polarity of the substituents has no significant impact on the sulfinyl route. This is also evident from the high molecular weights obtained in the actual polymerization of **6** ($M_w = 2.51 \times 10^5$ g/mol; Section 2).



Scheme 2. General scheme of the synthesis of **A**–**D** via the Mitsunobu reaction.

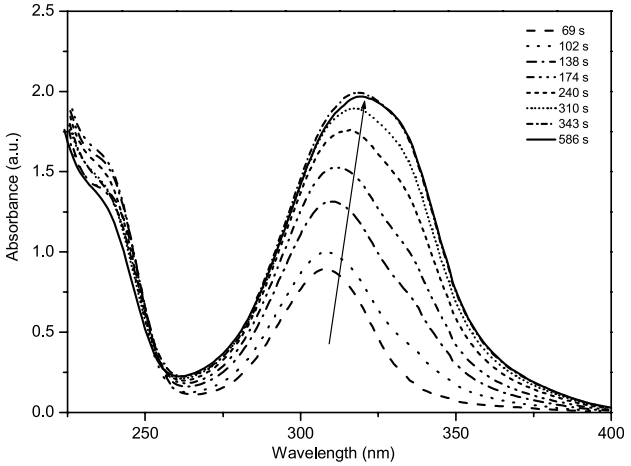


Fig. 1. Solution UV–vis absorption spectra (solvent 2-BuOH) of the gradual formation of the *p*-quinodimethane system **10** ($\lambda_{max}=320$ nm) during the polymerization of monomer **5**.

3.2. Thermal conversion of the precursor polymer to the conjugated structure

The final step in the sulfinyl precursor route is the thermal elimination of the sulfinyl group as a result of which the precursor polymer converts into the conjugated structure. Conjugated polymer **7** was prepared via two methods, i.e. thermal conversion in a thin film (**7a**) and thermal conversion in solution (**7b**). Polymer **7a** was specifically prepared to study the elimination process of the sulfinyl groups by in situ UV–vis spectroscopy in a thin film. At room temperature, thin films of the precursor polymer exhibit a strong absorbance with a maximum at $\lambda_{max}=300$ nm (Fig. 2). Upon heating from room temperature to 250 °C, a new absorption band appears which is associated with the conjugated system. During the elimination process, this band exhibits a gradual red shift ($\lambda_{max}=$ 470 nm at 110 °C) with increasing temperature due to an increase of the average conjugation length (Fig. 2). When the absorbance at this maximum wavelength ($\lambda_{max}=$ 470 nm) is monitored versus temperature, it is evident that the conjugated structure starts to develop around 75 °C. From Fig. 2 it is evident that the elimination process of a thin film of **6** heated at 2 °C/min to 110 °C is incomplete (i.e. residual absorption of **6** at $\lambda_{max}=300$ nm remains present). Apparently the presence of elimination products in the thin film results in an incomplete conversion and either a slower heating rate at this temperature or a higher temperature is required to complete the thin film process. Notwithstanding, the elimination can successfully be performed in toluene solution at 110 °C. After a double elimination, **7b** was obtained in excellent yield and UV–vis spectroscopy of solutions of **7b** revealed that the elimination was virtually complete (Fig. 3; only minimal absorption of **6** at $\lambda_{max}=$ 300 nm remains). Hence, for all further chemical conversions only **7b** was used.

Polymer **7b** exhibits all characteristics typical for alkoxy-substituted PPV derivatives, indicating that the incorporation of polar groups does not lead to significant problems in the solution elimination process. The solution UV–vis absorption maximum of **7b** is $\lambda_{max}=479$ nm (THF). The apparent molecular weight of **7b** as obtained by analytical SEC (2.90×10^5 g/mol, Section 2) is slightly higher than that of the precursor polymer **6**, as a result of the increase in hydrodynamic volume of **7b** due to the rigidity of its conjugated backbone. This increased rigidity is also reflected in the T_g of **7b** (55 °C), which is substantially higher than the T_g of **6** (−39 °C).

Polymer **7b** exhibits a typical thermochromic effect, which is clearly visible in the temperature dependent UV–vis absorption spectra (Fig. 4). Whereas at room temperature the absorption maximum of **7b** in a thin film is positioned around $\lambda_{max}=510$ nm, upon increase of temperature a reversible shift is observed to lower wavelength (i.e. $\lambda_{max}=470$ nm at 110 °C). The same phenomenon is

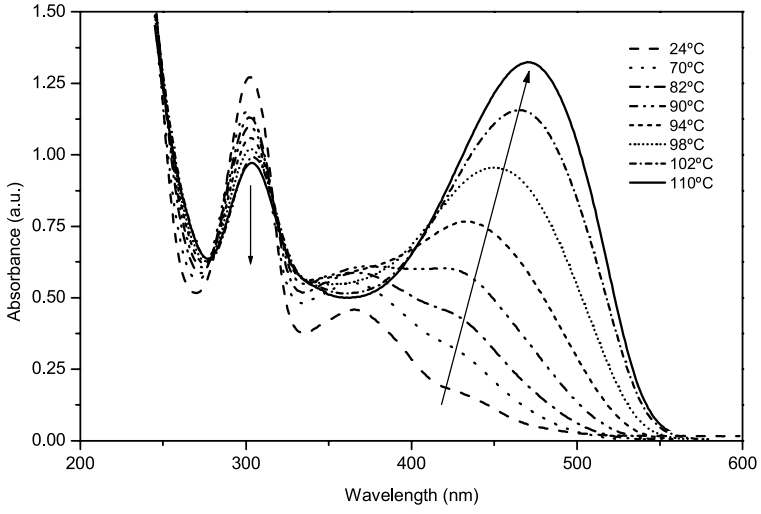


Fig. 2. Thin film UV–vis absorption spectra of the gradual formation of the conjugated polymer **7a** at selected temperatures.

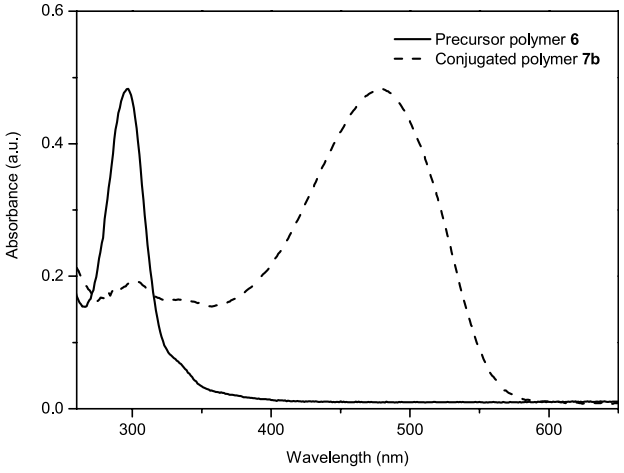


Fig. 3. Solution UV–vis absorption spectra of polymers **6** and **7b** (solvent THF).

observed with FT-IR spectroscopy where the double bond signal at 970 cm^{-1} decreases upon heating and increases to its initial value when the sample is cooled to room temperature. An additional heating/cooling experiment was performed to study the thermal degradation process of **7b**. From the UV–vis spectra it is evident that the conjugated structure exhibits thermal stability up to only 160 °C, whereas for example, alkoxy substituted PPV derivatives are stable up to 190 °C [24]. Notwithstanding, thermal stability up to 160 °C is sufficiently high for virtually all applications.

3.3. Hydrolysis of *7b* to *8*

Polymer **7b** was hydrolyzed using a base (K*t*BuO) giving **8** in excellent yields. The molecular weight of **8** (2.23×10^5 g/mol, Section 2) is only slightly lower than that of **7b**, indicating that the conjugated system does not degrade during hydrolysis. This is also corroborated by the solution UV–vis absorption spectrum of **8**, which exhibits a distinct transition at $\lambda_{max}=490$ nm (solvent DMSO), which is similar to that of **7b**. Furthermore, the T_g of **8** ($T_g=51$ °C) remains virtually unchanged as compared to **7b**.

It is noteworthy that previous researchers have claimed the successful synthesis of **8** using the Gilch precursor route, albeit without documenting the polymer properties and analytical data [21,25]. The only evidence provided in these reports for the existence of the carboxy-substituted PPV is a thin film UV–vis absorption spectrum, displaying a broad band with a shoulder at 430 nm [21]. In marked contrast polymer **8** displays a well defined transition at $\lambda_{max}=$ 490 nm in solution (solvent DMSO) and at the same wavelength in a thin film (Fig. 5). This further supports the versatility of the sulfinyl precursor route in the synthesis of polar substituted PPV derivatives. In addition, this improvement in optical properties, exemplifies the importance of precursor routes in general, to obtain high purity conjugated polymers.

Additional analyses have been carried out to verify the complete hydrolysis of the ester side groups. FT-IR spectroscopy of polymer **7b** shows a strong absorption band at 1728 cm^{-1}, which is characteristic of the carbonyl absorption of the ester side group. As the polymer **7b** is hydrolyzed into the desired carboxy-substituted polymer **8**, the peak shifts to 1709 cm^{-1}, characteristic of the carbonyl absorption of the carboxylic acid (Fig. 6). In addition, a broad band at approximately 2800 cm^{-1} is observed for the OH-stretch of the hydrogen bonded carboxylic acid groups of **8**. The complete hydrolysis of **7b** is even better observed using quantitative ^{13}C NMR. Whereas methylesters exhibit a distinct resonance at $\delta=$ circa 50 ppm (O–CH_3), this resonance is entirely absent in the hydrolyzed polymer **8**.

3.4. Post-polymerization functionalization via the Mitsunobu reaction

The carboxylic acid function of polymer **8** readily reacts with alcohol functionalized molecules under the mild conditions (room temperature) of the Mitsunobu reaction

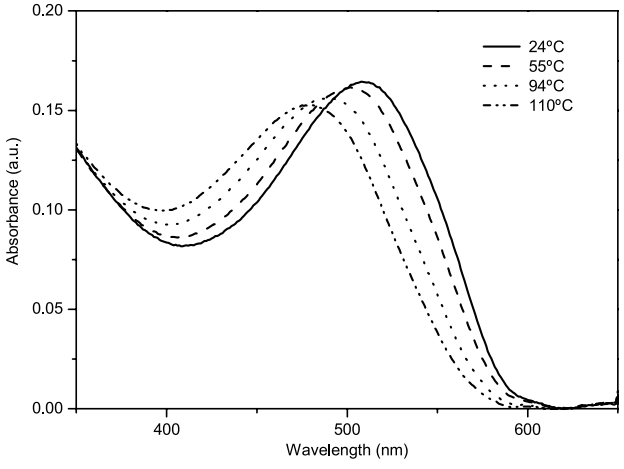


Fig. 4. Thin film UV–vis absorption spectra of polymer **7b** demonstrating the thermochromic effect.

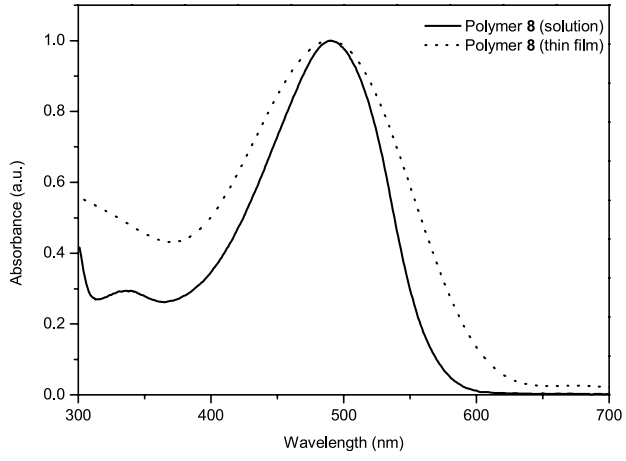


Fig. 5. Solution (DMSO) and thin film UV–vis absorption spectra of **8**.

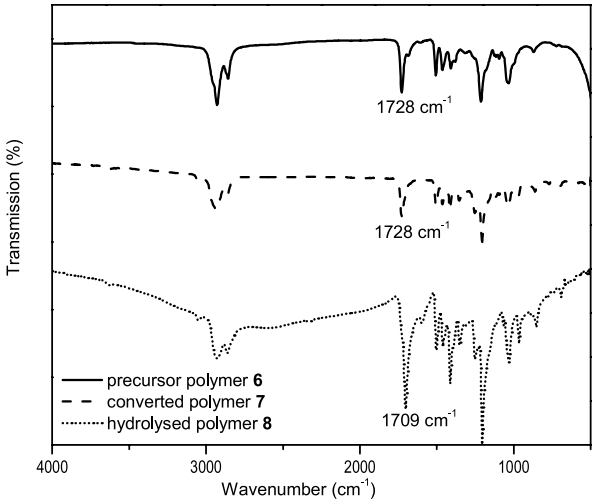


Fig. 6. FT-IR spectra of the sulfinyl precursor polymer **6**, the conjugated polymer **7b** and the hydrolyzed polymer **8**.

leading to the corresponding esters. This approach was tested with four hydroxy-bearing compounds giving substituted polymers **A**, **B**, **C** and **D** (Scheme 2). The solubility of **A**–**D** is limited, with polymer **D** being entirely insoluble in common organic solvents. The successful conversion is readily visible in the ^{1}H NMR spectra of the soluble polymers **A**, **B** and **C**. For all three polymers, a characteristic peak is found around $\delta = 5.1$–5.4 ppm, for the protons of the –COOCH_2-R groups. In addition, all characteristic peaks for the attached substituents are present. Although the ^{1}H NMR peaks are broad due to the polymeric nature of **A**–**C**, integration of the signals is consistent with a quantitative conversion of the carboxylic acid functionalities to the corresponding esters. The post-polymerization functionalization of **8** was further confirmed by comparison of the FT-IR-spectra. As shown in Fig. 7, the carbonyl absorption at 1709 cm^{-1} of the carboxylic acid, shifts to higher frequency upon formation of the ester bond in **A**–**D**.

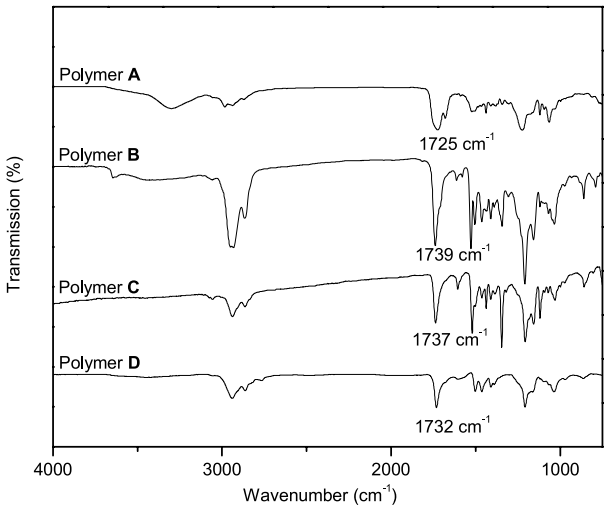


Fig. 7. FT-IR spectra of the polymers **A**, **B**, **C** and **D**.

In addition, it should be noted that in the FT-IR spectra of **A**–**D** the broad band at 2800 cm^{-1} of the OH-stretch has entirely disappeared. Hence, all FT-IR spectra are consistent with a full conversion of the carboxylic acid functionalities.

The apparent molecular weights as observed by SEC of **A**, **B** and **C** (1.29, 5.09 and 1.82×10^4 g/mol, respectively, Section 2) are lower than found for **8** (2.23×10^5 g/mol, Section 2). However, it should be noted that strong tailing is observed in the SEC analysis indicating that **A**–**C** exhibit interactions with the SEC column. Such interactions would result in a lower apparent molecular weight. Hence, these apparent molecular weights are unsuitable to judge the presence or absence of substantial polymer degradation during the Mitsunobu reaction. To resolve this issue, two additional experiments were performed. In the first experiment, OC_1C_{10}–PPV, which does not contain the carboxylic acid functionality, was subjected to the same Mitsunobu conditions as were used for the preparation of **C**. A SEC analysis before and after this treatment yielded no significant changes in the molecular weight of OC_1C_{10}–PPV, indicating that the conjugated structure of OC_1C_{10}–PPV was not affected by the reaction conditions. In a second experiment, polymer **A** was subjected to basic hydrolysis. Analytical data confirmed the full hydrolysis of the ester group, giving back the carboxylic acid substituted polymer **8**. Analytical SEC of this recovered **8** exhibits an increase in apparent molecular weight as compared to **A**, although the final molecular weight remains lower than that observed for the original **8**. Notwithstanding, this increase in apparent molecular weight further corroborates our observation that the anomalous analytical SEC results of **A**–**C** are likely the result of column interactions during SEC analysis.

To further confirm the presence of the conjugated system in **A**–**C**, UV–vis solution spectra were made (Fig. 8). The shape and peak positions of λ_{max} are strongly dependent on the solvent used as a result of solubility issues. In THF solution for **A**–**C** well defined transitions are observed at $\lambda_{max} = 469$, 488 and 486 nm, respectively, which is in the same spectral region as the transition observed for **8**. This

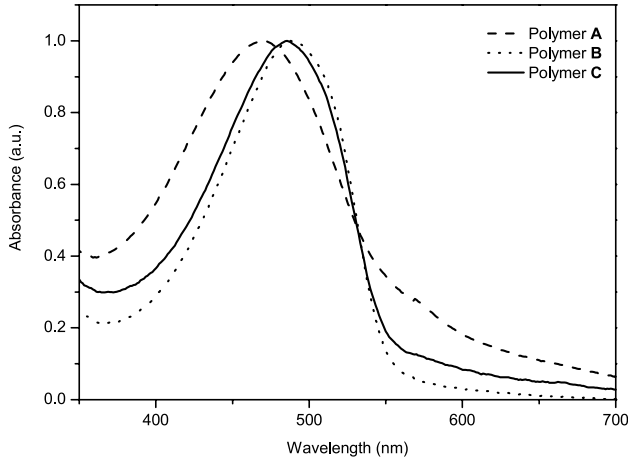


Fig. 8. Solution UV–vis absorption spectra of **A**, **B** and **C** (solvent THF).

observation further corroborates our finding that no substantial degradation of the conjugated system occurs during the Mitsunobu reaction.

4. Conclusions

In conclusion, the synthesis of poly(1,4-(2-(5-carboxy-pentyloxy)-5-methoxyphenylene)vinylene) **8** has been demonstrated. Polymer **8** has been obtained by quantitative hydrolysis of the corresponding ester-substituted PPV derivative **7b**, which was prepared via the sulfinyl precursor route. This demonstrates that the sulfinyl route is an excellent method to obtain PPV-derivatives with polar side groups. Polymers **7b** and **8** have been fully characterized using different analytical techniques as well as UV–vis absorption spectroscopy. Polymer **8** is soluble in common organic solvents, such as DMSO, acetone, THF and even in basic water. Furthermore, polymer **8** exhibits a significantly improved λ_{max} value as compared to previous reports, indicating its improved purity and lower defect levels. Polymer **8** forms an excellent starting platform to obtain polar functionalized PPV derivatives with more complex tailored substituents via post-polymerization functionalization of the carboxylic acid side group. Using the Mitsunobu reaction conditions substituents containing various ester groups, i.e. 4-nitrobenzyl, 2-nitrobenzyl, 5-(methyl)furfural and 3-*N*,*N*-dimethylamino-1-propane, have been covalently attached to the PPV backbone. Future work will focus on the scope of the post-polymerization functionalization reaction as well as the physical and chemical properties of the obtained novel polymers.

Acknowledgements

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