Polymerization Behavior of Xanthate-Containing Monomers toward PPV Precursor Polymers: Study of the Elimination Behavior of Precursor Polymers and Oligomers with in-Situ FT-IR and UV−Vis Analytical Techniques

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ABSTRACT: We have prepared two xanthate precursor polymers (**6**) and one sulfinyl precursor oligomer (**7**). In this way the polymerization behavior of three xanthate-containing monomers (**3**, **4**, and **5**) was studied. The chemical modifications on the monomer stage allowed to evaluate the outcome of the polymerization in relation to the chemical structure of the monomer. Polymerizations were performed in dry THF at different temperatures. The thermal conversion to the conjugated PPV structure, as well as its stability, was studied with different analytical techniques such as in-situ FT-IR spectroscopy, in-situ UV−vis spectroscopy, thermogravimetric analysis (TGA), and direct insert probe mass spectroscopy (DIP-MS). By combining the information obtained from these techniques, we were able to obtain a very detailed picture about the elimination process. These measurements also confirmed the formation of *cis* double bonds in xanthate precursor polymers on conversion. However, subsequent *cis*−*trans* isomerization in the end leads toward an *all-trans*-PPV polymer.

Introduction

Over the past decades conjugated polymers evolved from a lab curiosity to commercial applications. Ever since Burroughes et al. discovered luminescence in PPV, the research to this polymer and its derivatives became increasingly important.[1] PPV can be synthesized in many different ways, usually from a precursor polymer which can be converted to the conjugated structure in-situ or in an additional conversion step. The Wessling route, the Gilch route, and the sulfinyl route are known examples of such precursor routes.[2−4] The precursor route to which the least attention was devoted to until now is the xanthate precursor route.[5,6] Nevertheless, the xanthate precursor route shows interesting prospects. In this precursor route a xanthate group is used as thermally eliminable group to yield the double bound. Son et al. reported higher external quantum efficiencies for xanthate prepared PPV compared to Wessling PPV.[5] They explained this phenomenon by the presence of more *cis* linkages in the conjugated polymer which causes shorter "effective conjugation lengths" and makes the material more amorphous. However, a recent publication by Burn et al. questions this explanation; they contribute the higher efficiencies to the absence of harmful interactions between elimination products and ITO in a LED where xanthate prepared PPV is used as active material.[6] It has been shown that hydrogen chloride which is produced during the elimination step in the Wessling and Gilch route reacts with ITO and thus reduces PL.[6−8]

This clearly shows the potential of the xanthate group in the synthesis of PPV and the importance of a controlled elimination reaction in a device structure.

We have already reported on the synthesis of PPV and some of its derivatives via the sulfinyl precursor route.[4,9,10] Of further interest to us was an evaluation of the possibilities the xanthate group offers in the synthesis of PPV. To serve this purpose, three different monomers, combining sulfinyl and xanthate functionalities (Scheme 1), were synthesized and polymerized. Once the precursor polymers were formed, the thermal conversion to the conjugated structure was studied with in-situ FT-IR spectroscopy, in-situ UV−vis spectroscopy, TGA, and DIP-MS.

Experimental Section

Materials. All chemicals were purchased from Aldrich or Acros and used without further purification unless otherwise stated. Tetrahydrofuran (THF) was distilled over sodium/benzophenone.

Characterization. ^{1}H NMR spectra were obtained in $CDCl_3$ at 300 MHz on a Varian Inova spectrometer using a 5 mm probe. Chemical shifts (δ) in ppm were determined relative to the residual $CHCl_3$ absorption (7.24 ppm). The ^{13}C NMR experiments were recorded at 75 MHz on the same spectrometer using a 5 mm broadband probe. Chemical shifts were defined relative to the ^{13}C resonance shift of $CHCl_3$ (77.0 ppm). Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) with a narrow polydispersity by size exclusion chromatography (SEC). Separation to hydrodynamic volume was obtained using a Spectra series P100 (Spectra Physics) equipped with a precolumn (5 μm, 50 mm × 7.5 mm, guard, Polymer Labs) and two mixed-B columns (10 μm, 2 × 300 mm × 7.5 mm, Polymer Labs) and a refractive index (RI) detector (Shodex) at 40 °C. SEC samples are filtered through a 0.45 μm filter. HPLC grade THF (p.a.) is used as the eluent at a constant flow rate of 1.0 mL/min. Toluene is used as flow rate marker. The molecular weight of the sulfinyl precursor oligomers **7** was also measured on a low-molecular-weight column (5 μm, 300 mm × 7.5 mm, 100 Å, Polymer Labs). The results obtained from these measurements are nearly identical to those obtained on the high-molecular-weight column.

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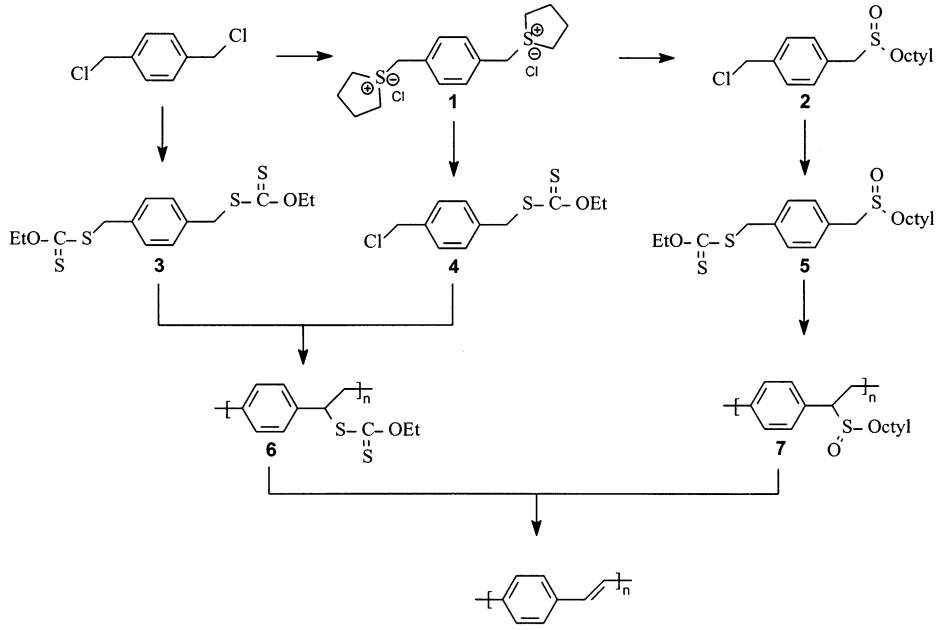
Scheme 1. Different Synthetic Pathways toward PPV



TGA measurements are performed on a TA instrument 951 thermogravimetric analyzer with a continuous nitrogen flow of 80 mL/min and a heating rate of 10 °C/min. Samples of precursor polymer (10 mg) are inserted in the solid state.

Direct insert probe mass spectroscopy analysis is carried out on a Finnigan TSQ 70, electron impact mode, mass range of 35−500. The electron energy is 70 eV. A $CHCl_3$ solution of precursor polymer is applied on the heating element of the direct insert probe. A similar heating rate of 10 °C/min was used to ensure a good comparison with TGA data.

The in-situ elimination reactions were performed in a Harrick high-temperature oven (purchased from Safir), which is positioned in the beam of a Perkin-Elmer spectrum one FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). The temperature of the sample is controlled by a Watlow (serial number 999, dual channel) temperature controller. The precursor polymer was spin-coated from a $CHCl_3$ solution (6 mg/mL) on a KBr pellet at 500 rpm. The spin-coated KBr pellet (diameter 25 mm, thickness 1 mm) is in direct contact with the heating element. All experiments were performed at 2 °C/min under a continuous flow of nitrogen. "Timebase software" supplied by Perkin-Elmer is used to investigate regions of interest.

In-situ UV−vis measurements were performed on a Cary 500 UV−vis−NIR spectrophotometer, specially adopted to contain the Harrick high-temperature cell (scan rate 600 nm/min, continuous run from 200 to 600 nm). Precursor polymer (**6** or **7**) was spin-coated from a $CHCl_3$ solution (6 mg/mL) on a quartz glass (diameter 25 mm, thickness 3 mm) 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 positioned in the beam of the UV−vis−NIR spectrophotometer, and spectra were taken continuously. The heating rate was 2 °C/min up to 300 °C. All measurements were performed under a continuous flow of nitrogen. "Scanning Kinetics software" supplied by Varian is used to investigate regions of interest.

Synthesis of 1,4-Bis(tetrahydrothiopheniomethyl)-xylene Dichloride (1) and 1-(Chloromethyl)-4-[(*n*-octylsulfinyl)methyl]benzene (2). These products were synthesized according to a procedure described elsewhere.[13]

Synthesis of 1,4-Bis[ethoxy(thiocarbonyl)thiomethyl]-benzene (3). This monomer was prepared by stirring a solution of 1,4-bis(chloromethyl)benzene (2.5 g, 0.0143 mol) and *O*-ethoxyxanthic acid potassium salt (5 g, 0.03125 mol) in methanol (50 mL) for 2 h at room temperature. The reaction mixture was poured into water, and the aqueous solution was extracted with chloroform and dried over magnesium sulfate. The filtrate was concentrated in vacuo and recrystallized from chloroform/hexane (10/90) and yielded product **3** as white needles (4.7 g, yield 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.27 (4H, s); 4.63 (4H, q, J = 7.2 Hz); 4.32 (4H, s); 1.40 (6H, t, J = 7.2 Hz) .^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 135.36; 129.53; 70.35; 40.22; 14.01. UV−vis (λ_{max}, CH_2Cl_2): 356 nm; mp 57.2−58 °C. FT-IR (KBr, cm^{-1}): 2980 (ν_{C-H} aliph), 1510−1397 (ν_{C-H} CH_3,CH_2), 1251 (*p*-phenylene CH out-of-plane bend), 1217−1107−1048 ($\nu_{SC(S)OCH_2CH_3}$), 688 (ν_{C-S}).

Synthesis of [1-Ethoxy(thiocarbonyl)thiomethyl-4-(chloromethyl)]benzene (4). *O*-Ethoxyxanthic acid potassium salt (2.96 g, 19 mmol) was solubilized in methanol (40 mL). The clear solution was added in one portion to a stirred solution of 1,4-bis(tetrahydrothiopheniomethyl)xylene dichloride (**1**) (10 g, 19 mmol) in methanol (100 mL). After 1 h the reaction mixture was neutralized with aqueous HCl (1 M) and concentrated in vacuo. The crude product was diluted with chloroform (200 mL), and the precipitate was filtered off. The filtrate was concentrated, and *n*-octane (75 mL) was added. The *n*-octane was concentrated in vacuo to remove tetrahydrothiophene. This sequence was repeated three times. The reaction mixture was purified using column chromatography (SiO_2, eluent: $CHCl_3$/hexane 50/50) (yield 64%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.32 (2H, s); 7.27 (2H, s); 4.60−4.67 (2H, q, J = 7.2 Hz); 4.55 (2H, s); 4.34 (2H, s); 1.38−1.42 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 137.87 (1C); 135.37 (1C); 129.53 (2C); 129.16 (2C); 70.39 (1C); 45.91 (1C); 40.18 (1C); 14.00 (1C). UV−vis (λ_{max}, CH_2Cl_2): 353 nm; mp 114.7−116 °C. FT-IR (KBr, cm^{-1}): 2980 (ν_{C-H} aliph), 1510−1397 (ν_{C-H} CH_3,CH_2), 1251 (*p*-phenylene CH out-of-plane bend), 1217−1107−1048 ($\nu_{SC(S)OCH_2CH_3}$),688 (ν_{C-S}).

Synthesis of 1-((*n*-Octylsulfinyl)methyl)-4-(ethoxy-(thiocarbonyl)thiomethyl)benzene (5). *O*-Ethoxyxanthic acid potassium salt (1.5 equiv) was added portionwise to a solution of 1-(chloromethyl)-4-[(*n*-octylsulfinyl)methyl]benzene (prepared as reported earlier)[13] (2 g, 6.6 mmol) in methanol (50 mL). The mixture was stirred for 12 h at room temperature. The reaction mixture was poured into water and extracted three times with chloroform. The organic layer was dried over magnesium sulfate and concentrated in vacuo to yield the pure product (**5**) (2.42 g, yield 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.32 (2H, d, J = 8.4 Hz); 7.20 (2H, d, J = 8.4 Hz); 4.61 (2H, q, J = 7.2 Hz); 4.32 (2H, s); 3.90 (2H, dd, J = 13.2 Hz); 2.52 (2H, t, J = 7.8 Hz); 1.70 (2H, m); 1.38 (3H, t, J = 7.2 Hz); 1.22 (10H, s(br)); 0.83 (3H, t, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 136.28 (1C); 130.46 (1C);

Table 1. Polymerization Results for the Different Monomers[a]

	temp (°C)	yield (%)	M_w ($\times 10^{-3}$)	PD
6 from **3**	−20	35	313	3.5
	0	34	300	2.6
	30	15	25	2.0
6 from **4**	−20	55	472	5.1
	0	26	272	5.5
	30	35	202	5.6
7 from **5**	0	23	1.6	1.3
	30	35	1.6	1.2
	50	65	1.6	1.3

[a] M_w and PD were determined by GPC vs PS standards using THF as eluent.

129.85 (2C); 129.51 (2C); 70.42 (1C); 58.02 (1C); 51.26 (1C); 40.16 (1C); 31.92 (1C); 29.37 (1C); 29.21 (1C); 29.04 (1C); 22.82 (1C); 22.68 (1C); 14.30 (1C); 14.01 (1C). UV−vis (λ_{max}, CH_2Cl_2): 355 nm; mp 81.4−82.8 °C. FT-IR (KBr, cm^{-1}): 2957−2918−2849 (ν_{C-H} aliph), 1511−1486−1419 (ν_{C-H} CH_3, CH_2), 1211−1117−1071 ($\nu_{SC(S)OCH_2CH_3}$), 1056−1025 (ν_{S-O}), 849 (1,4-subst arom).

Synthesis of the Precursor Polymer (6 and 7). All polymerizations were carried out under the same conditions in dry tetrahydrophuran (THF, dried over sodium with benzophenon) at different temperatures (Table 1). Solutions of monomer (1 mmol in 6.5 mL of THF) and base (potassium *tert*-butoxide; 1.05 mmol in 3.5 mL of THF) were prepared and degassed for 1 h by a continuous flow of nitrogen. The base solution was added in one portion to the stirred monomer solution. During the reaction the temperature was kept constant, and the passing of nitrogen was continued. After 1 h the reaction mixture was poured into well-stirred ice water whereupon the polymer precipitated. The water layer was extracted with chloroform to ensure that all polymer and residual fraction were collected, and the combined organic fractions were concentrated in a vacuum. The polymer was precipitated in cold diethyl ether/hexane (1/1; 100 mL; 0 °C), collected by filtration, and dried in a vacuum. The residual diethyl ether/hexane fraction was concentrated in a vacuum. GPC was performed in THF vs polystyrene standards. Polymerization results are summarized in Table 1. The rest fractions only contain monomer residues.

Precursor Polymer 6. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.90−6.99 (4H); 4.79 (1H); 4.51 (2H); 3.27 (1H); 3.05 (1H); 1.29 (3H).^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 213.97 (1C); 137.68−137.35 (2C); 129.27 (2C); 127.88 (2C); 69.78 (1C); 55.28 (1C); 41.97 (1C); 13.67 (1C). FT-IR (KBr, cm^{-1}): 2980, 1510, 1397, 1251, 1217, 1107, 1048, 688.

Precursor Oligomer 7. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.80−7.50 (4H); 3.25−3.99 (2H); 2.39−2.78 (1H); 1.95−2.23 (2H); 1.45−1.75 (2H); 1.11−1.42 (10H); 0.75−0.9 (3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 137.87; 130.10; 129.66; 129.30; 128.88; 128.58; 126.48; 70.02; 65.32; 57.67; 50.89; 49.65; 49.27; 36.02; 31.51; 28.97; 28.80; 28.69; 22.84; 22.40; 13.92. FT-IR (KBr, cm^{-1}): 2957, 2918, 2849, 1511, 1486, 1419, 1056, 1025.

Conjugated Oligomer 8. This compound was made from the precursor oligomer **7** by heating a film of **7** (30 mg in 2 mL of $CHCl_3$ and allow the $CHCl_3$ to evaporate) at 100 °C for 3 h under vacuum. ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 137.45; 130.42; 129.08; 127.01; 57.99, 50.92; 31.76; 29.21; 29.04; 28.87; 22.65; 22.46; 14.14. FT-IR (KBr, cm^{-1}): 3025, 1511, 956, 858, 834. UV−vis spectra of the conjugated oligomer **8** were taken in toluene at room temperature (λ_{max} at 327, 341, 364, and 390 nm). For comparison, the spectrum of *trans*-stilbene (purchased from Aldrich and used as received) was also taken in the same conditions (λ_{max} = 328 nm).

Results and Discussion

Monomer Synthesis and Polymerization Reactions. In the literature, monomers used in the xanthate precursor route are synthesized from a dihalogenide in a single step reaction.[5] Usually the *O*-ethyl xanthatic group is used. A drawback of the xanthate precursor route is the rather strict way in which the polymerization has to be carried out. Dry THF is needed as a solvent, and the polymerization temperature must be sufficiently low to get good polymerization yields and high-molecular-weight polymers. In the sulfinyl precursor route, the polymerization conditions are less strict, and polymerizations can proceed in a wide range of solvents at different temperatures.[9] Another advantage of the sulfinyl precursor route is the broad scope of PPV derivatives that can be synthesized whereas for the xanthate precursor route, so far, only a few PPV derivatives have been reported.[5,6,11,12] Another point worth mentioning is the fact that a sulfinyl group generally eliminates at lower temperatures compared to the xanthate group.

However, we have an interest in exploring both xanthate and sulfinyl precursor routes toward the synthesis of PPV in order to get a better understanding of the influence of the eliminable group on the properties of the final conjugated polymer. For this purpose, three different monomers (**3**, **4**, and **5**) were synthesized. All monomers consist of a 1,4-xylene unit to which different groups (xanthate, chlorine, or sulfinyl) are attached. In the traditional symmetrical bisxanthate monomer **3** there is no chemical differentiation between polarizer and leaving group. In monomer **4** one xanthate group is replaced by a chlorine atom, and in monomer **5** a sulfinyl group is introduced. These chemical modifications also allow to evaluate the outcome of the polymerization in relation to the chemical structure of the monomer.

The different synthetic pathways to PPV are shown in Scheme 1. The bisxanthate monomer **3** was synthesized from its dichloro analogue whereas the monoxanthate monomer **4** was synthesized departing from a bis(sulfonium) salt **1**. This approach is similar to the one used in the synthesis of compound **2** and proved necessary to obtain monoxanthate **4** in a highly selective way.[13] Attempts to make compound **4** directly from the dichloride were less selective, and a difficult chromatographic separation had to be carried out to separate the different products formed in this reaction. The sulfinyl−xanthate monomer **5** was synthesized by reacting compound **2** with potassium *O*-ethylxanthic acid salt.

These three monomers (**3**, **4**, and **5**) were all polymerized in the same "standard" conditions (Experimental Section). Each monomer was polymerized at three different temperatures, and dry THF was used as a solvent in all polymerization reactions. Potassium *tert*-butoxide was used as a base and was added in solution in a slight excess of 1.05 equiv. The polymerization time was 1 h, after which the reaction mixture was poured into ice water. The polymer was extracted with chloroform, concentrated, and precipitated in diethyl ether/hexanes. The precursor polymers were soluble in organic solvents such as chloroform and THF.

Molecular weights and polydispersities were determined by gel permeation chromatography (GPC) vs polystyrene standards (eluent THF). Monomers **3** and **4** were polymerized to the xanthate precursor polymer **6** at −20, 0, and 30 °C. The spectral data for these polymers are consistent with those in the literature.[5,11] Monomer **3** could only be polymerized to high-molecular-weight polymer at temperatures equal to or lower than 0 °C whereas in the case of monomer **4** high-molecular-

weight polymers were obtained at all temperatures tested (Table 1). Polymerization yields vary from rather low to good, but no clear trend could be observed. Note that the polydispersities of the precursor polymers obtained from monomer **4** are significantly higher than those obtained for the polymerization of monomer **3**. From Table 1 we observe an inverse relationship between the molecular weight and the temperature at which the polymerization is performed. Decreasing the temperature in both cases leads to higher molecular weights. This observation is in accordance with our experience in the polymerization of monomer **2** in the sulfinyl precursor route. On the other hand, within a certain temperature domain (0−60 °C), the polymerization yield for monomer **2** proved almost independent of temperature.[14] This is in contrast with the data obtained for the polymerization of the bis(xanthate) monomer.

Monomer **5** was polymerized at 0, 20, and 50 °C. For this monomer higher polymerization temperatures were needed to keep the reagents soluble. To our surprise, all polymerizations of monomer **5** only yielded oligomers of precursor **7**. GPC showed these oligomers all had very similar molecular weights. ^{1}H and ^{13}C NMR spectroscopies clearly showed different signals for the sulfinyl groups in the main chain compared to those situated at the end of the oligomer chain. Moreover, the similar integration of both signals suggests both sulfinyl groups exist for approximately an equal amount. Increasing the polymerization temperature left the molecular weight unchanged, but the polymerization yield increased significantly (Table 1). Combination of a xanthate group and a sulfinyl group in the same monomer apparently limits the polymerization capabilities. Probably, the quinoid structure is not formed rapidly enough in concentrations that are necessary to obtain high-molecular-weight polymer. Further research is needed here to reveal the exact nature of the phenomena that take place.

Thermal Conversion of the Xanthate Precursor Polymer (6) to the Conjugated Structure. The final step in both the sulfinyl and xanthate precursor route is a thermal elimination reaction to form the double bond. In the latter the xanthate group is eliminated by a modified Chugaev reaction to yield the double bond. The xanthate group is attached to the polymer backbone via the sulfur atom instead of the oxygen atom in a normal Chugaev reaction. This effectively lowers the elimination temperature and also simplifies the monomer synthesis.[5] The elimination products that are liberated during elimination are unstable and further react to form ethanol and carbon disulfide on one hand and ethanethiol and carbonoxy sulfide on the other.[15,16]

For comparison, in the sulfinyl precursor route the elimination process is an expulsion of sulfenic acid and the formation of a double bond on the polymer backbone. The double bond formed is mainly *trans* due to increased steric hindrance in the transition state which leads to the *cis* configuration. The sulfenic acids which are split off are unstable and dimerize immediately to give water and thiosulfinates, which finally disproportionate to yield thiosulfonates and disulfides.[17] In general, the conversion to the conjugated structure, as well as its thermal stability, can be studied by different techniques. The ones used here are in-situ FT-IR spectroscopy, in-situ UV−vis-spectroscopy, TGA, and DIP-MS.

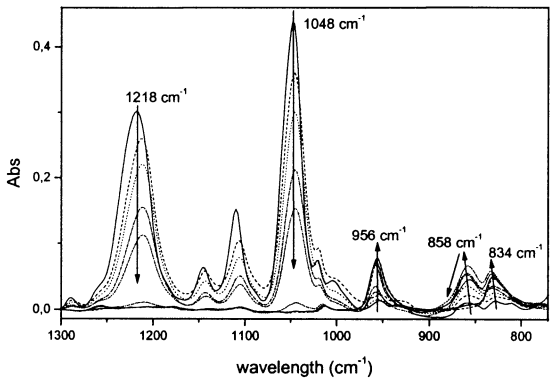


Figure 1. Enlarged part of the IR spectrum at different temperatures (24, 145, 160, 170, 190, 205, 235, 295, and 340 °C).

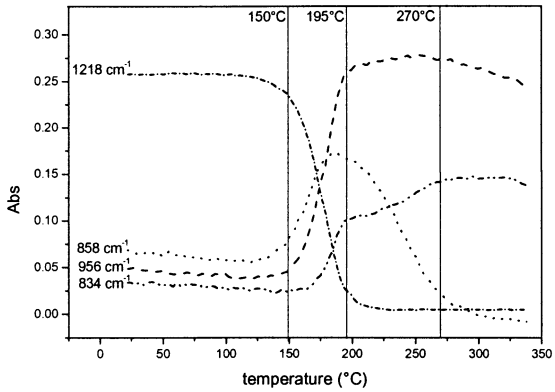


Figure 2. Absorptions at 834, 956, 858, and 1218 cm^{-1} vs temperature.

The thermal elimination and stability of the xanthate precursor polymers (**6**) were examined and proved to be similar for all xanthate precursor polymers independent of the monomer (**3** or **4**) and polymerization temperature used. For simplicity reasons, only the graphs of the thermal behavior of precursor polymer **6** prepared from monomer **3** at 0 °C are shown.

In-situ FT-IR spectroscopy measurements were carried out on film, spin-coated on KBr pellets. An experimental setup was used (see Experimental Section) which allowed in-situ monitoring of the elimination process. A nonisothermal heating program of 2 °C/min up to 340 °C under a continuous flow of nitrogen was used. Figure 1 shows an enlarged part of the IR spectrum at a few selected temperatures.

The xanthate precursor polymer **6** shows strong absorption bands at 1218 and 1048 cm^{-1}; both arise from the *O*-ethyl xanthate leaving group. When the elimination progresses, a new absorption signal appears at 956 cm^{-1} that originates from the *trans*-vinylene double bond. The absorption signals from the xanthate group gradually disappear with increasing temperature. The absorption at 858 cm^{-1} is assigned to the formation of some *cis* linkages in the conjugated structure.[5,12] No *cis* double bonds can be detected after conversion of a sulfinyl precursor polymer.[17] In Figure 2, the evolution of the absorbance of the most important signals is visualized as a function of temperature. In this way the relative trends in elimination behavior become clear.

Both elimination of the xanthate group and formation of the *cis* and *trans* double bond start around 150 °C. Between approximately 195 and 270 °C the signal of the *cis*-vinylene double bond at 858 cm^{-1} decreases

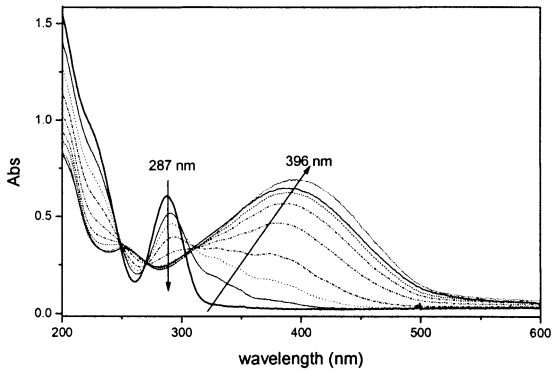


Figure 3. UV−vis spectra of the gradual formation of the conjugated structure at a few selected temperatures (35, 160, 170, 180, 185, 195, 230, and 270 °C).

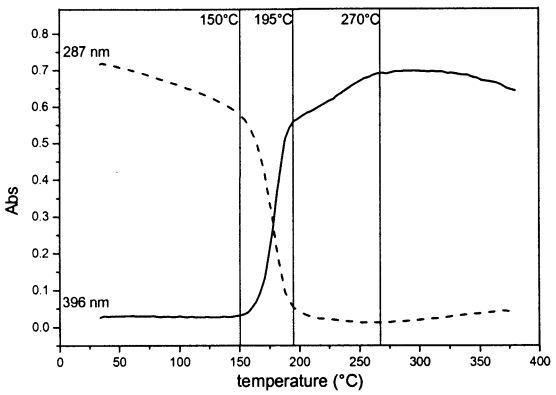


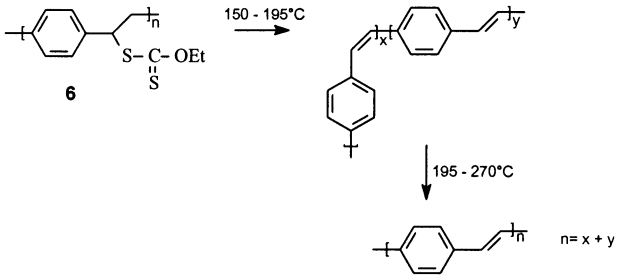
Figure 4. Absorption at 287 and 396 nm vs temperature.

again while the signal of the *trans*-vinylene double bond (956 cm^{-1}) slightly increases in this temperature domain. This phenomenon is interpreted as an isomerization process of the *cis* double bonds into the thermodynamically more favorable *trans* double bonds. The signal of the *p*-phenylene C−H out-of-plane deformation at 834 cm^{-1} also increases during the elimination process.[15]

In-situ UV−vis spectroscopy measurements were carried out on film, spin-coated on quartz. The heating setup was identical as for the FT-IR measurements, and a nonisothermal heating program of 2 °C/min up to 380 °C under a continuous flow of nitrogen was used. Before heating, an absorption band from the xanthate precursor polymer (**6**) is present (λ_{max} at 287 nm). As the heating program progressed, a new absorption band appeared that red shifts with increasing temperature (Figure 3). At higher temperatures the fine structure disappears, and the absorption band broadens to cover the various oligomer bands. At 270 °C, the absorption reaches its maximum value, and a conjugated PPV polymer with an absorption maximum around 396 nm is obtained. This peak maximum is blue-shifted compared to a PPV polymer prepared via the sulfinyl precursor route.[4] This result may point to the fact that the PPV prepared via the xanthate precursor route has more chemical defects present in the structure compared to the sulfinyl prepared PPV.

When the absorbance at 396 nm is plotted vs increasing temperature (Figure 4), it is clear that the absorption spectrum develops in two steps: a first step between 150 and 195 °C (fast) leading to a λ_{max} value of 386 nm and a second step between 195 and 270 °C (slower) which yields a final value of λ_{max} equal to 396 nm. The first step coincides with the decrease in IR of the xanthate signal, and this indicates that upon elimination of the xanthate group the "effective conjugation length" is limited by the simultaneous formation of *cis* and *trans* double bonds in the backbone of the conjugated system. The second step leads to an increase of "effective conjugation length" demonstrated by the red shift of λ_{max} and coincides with the decrease of the signal in IR of the *cis* double bonds. This is consistent with the interpretation from the IR data that a *cis*−*trans* isomerization is responsible for the decrease of the *cis* double bond signal in IR in the temperature range of 195 and 270 °C.

Scheme 2. Schematical Overview of the Elimination Reaction and *Cis*−*Trans* Isomerization of PPV Prepared via the Xanthate Precursor Route



Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min in a nitrogen atmosphere. The sample was heated from ambient temperature to 600 °C. Two major steps of weight loss are visible. The first (180−330 °C) is due to the elimination of the xanthate group and evaporation of the elimination products. The second period of weight loss (520−600 °C) accounts for the degradation of the polymer backbone.

The elimination was also studied by DIP-MS, with an identical heating rate of 10 °C/min (as used in TGA experiments) under vacuum conditions (10^{-6} mmHg), to analyze the elimination products. For this technique, the precursor polymer is placed directly on the heating element of the probe. Two signals were observed: one can be assigned to an elimination step (184−330 °C) and the other one to a degradation step (420−565 °C). There is no difference in elimination temperature observed in TGA (nitrogen atmosphere) and DIP-MS (vacuum), e.g., maximum at 242 °C. This implies that at this temperature the elimination products that are liberated will evaporate immediately, even in a nitrogen atmosphere under normal pressure. These TGA and DIP-MS data for the xanthate precursor polymers differ from those obtained for sulfinyl precursor polymers because the elimination reaction itself and the evaporation of the elimination products are kinetically separated in the latter.[17] The elimination temperature observed with these techniques is higher than that obtained from the in-situ UV−vis and in-situ FT-IR results. This difference is attributed to the difference in heating rate.

From the combined measurements it is concluded that elimination of the xanthate precursor polymer **6** toward a PPV polymer when performed beneath 195 °C will lead to a mixed *cis*−*trans* configuration. To obtain an *all-trans*-PPV structure, the conversion should be done at a temperature around 250 °C. At both these temperatures all elimination products will immediately evaporate, and degradation does not yet occur (Scheme 2). Furthermore, from the isothermal experiment at 250 °C it became clear that an *all-trans*-PPV polymer is obtained after less than 2 h. This means that it is not

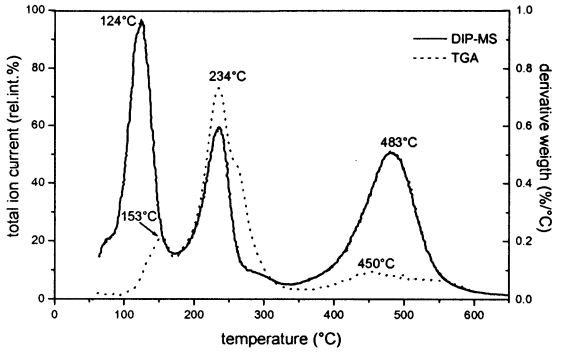


Figure 5. TGA thermogram (dotted line) and DIP-MS thermogram (solid line) of the sulfinyl oligomer (**7**).

necessary to do the conversion for 15 h or more on 250 °C, like often mentioned in the literature.[6]

Thermal Conversion of the Sulfinyl Precursor Polymer 7. The study of the thermal elimination and stability of precursor polymer **7** shows quite different results because here a sulfinyl group is eliminated to yield the double bond. In general, much lower temperatures are needed to convert a sulfinyl precursor polymer to the conjugated structure compared to the xanthate precursor polymer.[18] As mentioned earlier, GPC showed that precursor polymer **7** is an oligomer, and the elimination and stability behavior of oligomers may be somewhat different from that of the corresponding polymers.[19] Indeed, in oligomer **7** a relatively large percentage of the sulfinyl groups act as end groups; this allows to study the thermal stability behavior of such sulfinyl end groups compared to the sulfinyl groups in the internal part of the oligomer backbone.

A first technique that was used to study the elimination and stability of oligomer **7** was DIP-MS. Three signals are observed in the thermogram (Figure 5). The first signal (76−167 °C) can be assigned to the elimination of the sulfinyl groups in the oligomer main chain that form the double bonds. The fragments analyzed by DIP-MS correspond to the expected thiosulfonate and disulfide elimination products. The second signal (174−276 °C), based on the fragments detected, is probably caused by the thermolysis of the sulfinyl groups at the end of the oligomer chain. Although similar fragments are observed, these two processes must chemically proceed via totally different mechanisms. Furthermore, out of the data, a kinetic separation between them is possible. The third signal (400−550 °C) in the thermogram accounts for the decomposition of the conjugated system.

In TGA also three signals are present (Figure 5). A first one with a maximum at 153 °C is caused by the evaporation of the elimination products. This signal appears at a higher temperature compared to the corresponding signal in DIP-MS (124 °C) because of the difference in atmosphere used in both techniques (vacuum in DIP-MS and nitrogen flow at normal pressure in TGA). A second signal in TGA with a maximum at 234 °C is assigned to the thermolysis of the sulfinyl end groups on the basis of the data in DIP-MS. This implies that the products that are liberated at this temperature will evaporate immediately. The third signal at higher temperatures corresponds to the degradation of the conjugated polymer.

The thermal stability of oligomer **7** was also studied with in-situ FT-IR spectroscopy. A nonisothermal experiment was carried out at 2 °C/min up to 275 °C under a continuous flow of nitrogen. In Figure 6 the IR spectra at four different temperatures (60, 100, 175, and 250 °C) are shown. At 60 °C the main absorptions arise from the sulfinyl stretching (1043 cm^{-1}) and from stretchings in the aliphatic region (2750−3000 cm^{-1}). When higher temperatures are reached, both these absorptions decrease strongly and a new absorption at 963 cm^{-1} appears which can be assigned to the *trans*-vinylene double bond. In this case, as in high-molecular-weight sulfinyl precursor polymers, no *cis* double bonds could be observed.[17] At 175 °C the sulfinyl absorption has disappeared completely, and a new signal appears at 1696 cm^{-1} which may correspond to the formation of aromatic aldehydes.[20]

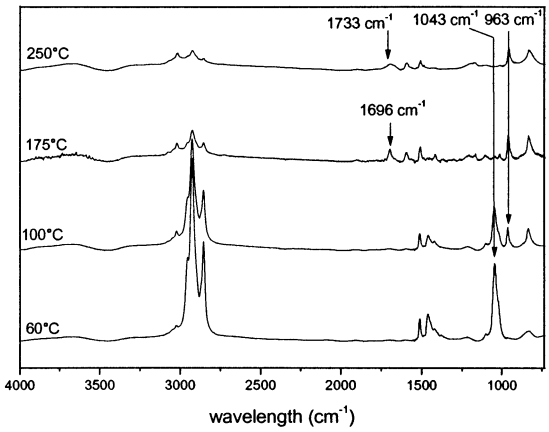


Figure 6. FT-IR spectra of the sulfinyl oligomer (**7**) at 60, 100, 175, and 250 °C.

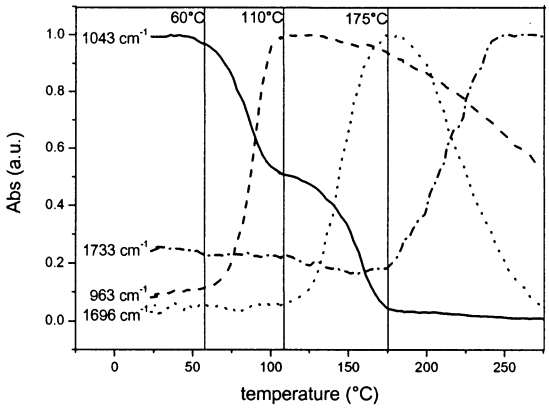


Figure 7. Absorptions at 963, 1043, 1696, and 1733 cm^{-1} vs temperature.

When these absorptions are plotted vs increasing temperature (Figure 7), the trends in elimination behavior of oligomer **7** become clear. The sulfinyl absorption (1043 cm^{-1}) decreases in two distinct steps. The first decrease takes place in a temperature domain between 60 and 100 °C and is caused by the elimination of the sulfinyl groups in the oligomer main chain as it coincides with the increase of the *trans*-vinylene double bond signal at 963 cm^{-1}, between 70 and 110 °C. The second step in the decrease of the sulfinyl absorption occurs between 130 and 175 °C. This second decline does not give rise to additional double bonds and thus has to originate from the thermolysis of the sulfinyl end groups. Note that the main-chain sulfinyl groups and the sulfinyl end groups have similar intensities which again suggests both sulfinyl groups are present for approximately an equal amount. As mentioned earlier, this was also confirmed by ^{13}C NMR spectroscopy.

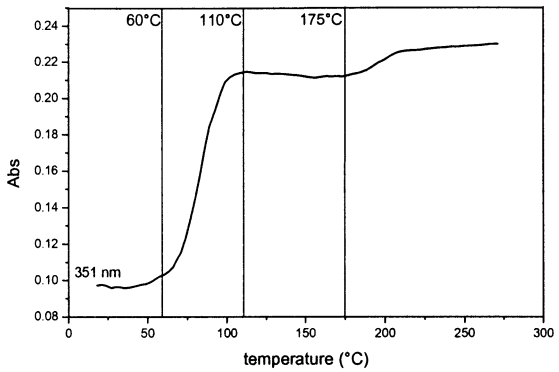
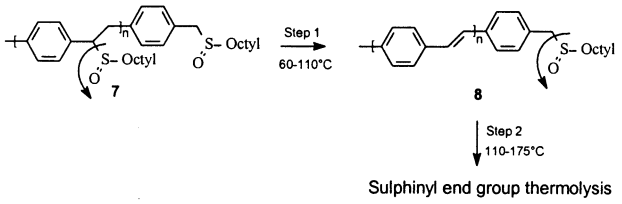


Figure 8. Absorption at 351 nm vs temperature.

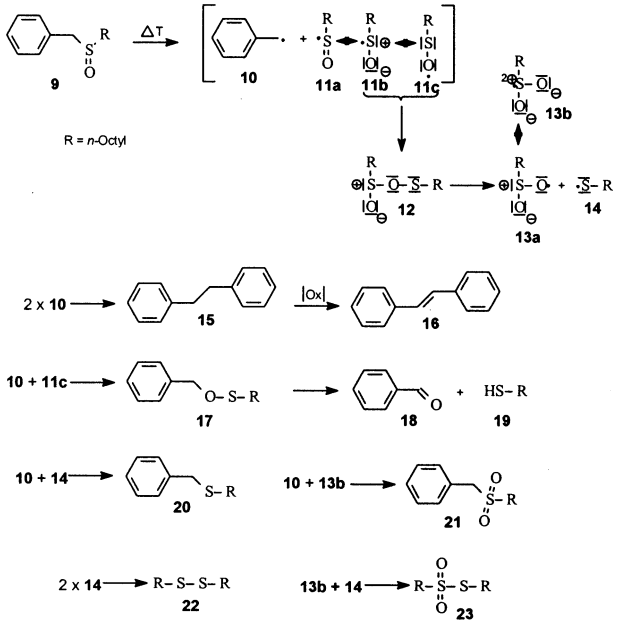
Furthermore, between 130 and 175 °C the absorption for the carbonyl stretching (1696 cm^{-1}) increases. This observation may indicate that an unidentified number of sulfinyl end groups is converted to carbonyl functionalities. At higher temperatures (175 °C) the absorption at 1696 cm^{-1} again decreases, and a new absorption band at 1733 cm^{-1} appears (Figure 6), which partially overlaps the signal at 1696 cm^{-1} and probably corresponds to higher oxidized products.

Before commenting on the origin and the mechanism of formation of these carbonyl functionalities, we will discuss the results of the same experiment performed with in-situ UV−vis spectroscopy. A nonisothermal heating program of 2 °C/min up to 270 °C under a continuous flow of nitrogen was used. Before heating, an absorption band at 324 nm is present from the precursor oligomer. After heating until 270 °C a conjugated oligomer with an absorption maximum at 351 nm is obtained. When the absorption at this maximum wavelength is plotted vs temperature, two steps can be visualized in the elimination process (Figure 8). Between 60 and 110 °C the sulfinyl groups in the oligomer main chain are eliminated, and a conjugated oligomer with an absorption maximum at 339 nm is formed. Starting from 175 °C, a second small increase in absorption can be observed, and eventually the maximum at 351 nm is reached. Remember that it was clear from the previous FT-IR experiment that both the sulfinyl main chain and the sulfinyl end groups had been eliminated completely at 175 °C. The second increase of the "effective conjugation length" observed in the UV−vis can therefore only be explained by a new subsequent process that follows the thermolysis of the sulfinyl end groups. Explaining the phenomenona observed during the thermolysis of the sulfinyl end groups was possible by combining literature data on the thermal and/or photochemical conversion of sulfinyl functionalities in general[21−23] and what is known on the dimerization and disproportionation behavior of sulfenic acids.[17] Mislow et al. suggested the benzylic C−S bond to be notable weak in benzyl sulfinyl compounds.[21,24] At elevated temperatures this may result in homolytic cleavage and formation of a radical pair. The same cleavage was also observed in photochemical experiments on benzyl sulfinyl compounds.[23] These papers also report the presence of benzaldehyde upon thermolysis or photolysis of benzyl sulfinyl compounds. This explains the formation of aldehyde functionalities as observed in the FT-IR experiment in the temperature domain between 110 and 175 °C. To clarify the second small increase in "effective conjugation length" observed in UV−vis above 175 °C, an additional experiment was

Scheme 3. Elimination and Thermolysis of the Different SulfInyl Groups in SulfInyl Precursor Oligomer 7



Scheme 4. Schematic Overview of the Formation of Products 15−23 upon Homolytic Cleavage of the C−S Bond in Compound 9



set up in which we mimicked the thermal behavior of the sulfinyl end groups. To do so, a model compound **9** was heated at 200 °C for 15 h, and the resulting reaction mixture was analyzed by GC-MS. A complex reaction mixture resulted, and products **15**−**23** were identified (Scheme 4). Once the weak C−S bond is broken, the radicals formed (**10**, **11a**−**c**) can recombine to yield several reaction products. Product **15** clearly arises from radical coupling of two benzyl radicals. Combination of two sulfinyl radicals (**11b** and **11c**) results in the formation of the unstable product **12**, which further disproportionates to form radicals **13** and **14**. Understanding the formation of benzaldehyde was possible by combining radicals **10** and **11c** to from the sulfenic ester **17**. Thermal decomposition of **17** can yield benzaldehyde **18** and thiol **19**. The other products in the reaction mixture arise from alternative recombination of the respective radicals (Scheme 4). The observed stilbene (**16**) is presumed to be formed by oxidation of dibenzyl **15**. Probably radical **11c** acts as an oxidizing agent in this reaction, yielding a sulfenic acid and consequently also **22** and **23**. Extrapolation of this result toward the thermal behavior of the oligomer **7** would lead to coupling of two oligomer chains followed by oxidation and thus an extension of the "effective conjugated system" which can account for the observed red shift in UV−vis spectroscopy at temperatures above 175 °C.

To demonstrate the kinetic separation in the elimination processes of the different sulfinyl groups present in oligomer **7**, an experiment was set up which should

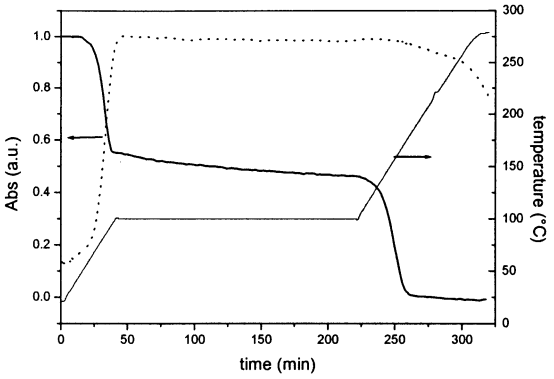


Figure 9. Absorptions at 963 cm^{-1} (dotted line) and 1043 cm^{-1} (solid line) as a function of time and temperature.

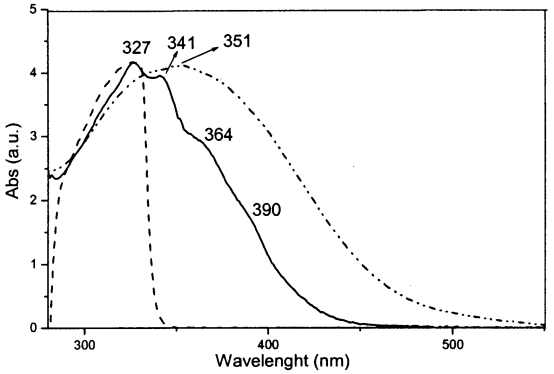


Figure 10. UV spectrum in toluene of the conjugated oligomer **8** (solid line) and *trans*-stilbene (dashed line) and the oligomer **8** in film (dash dotted line) after heat treatment until 270 °C.

allow the sulfinyl groups, that give rise to double bonds, to be eliminated selectively whereas the sulfinyl end groups are left unchanged. In-situ FT-IR spectroscopy was used to monitor the elimination process. In this experiment the sample was heated at 2 °C/min until 100 °C, kept at this temperature for 3 h, and then heated further until 300 °C at 2 °C/min. In Figure 9 this temperature program is shown next to the intensity profiles for the signal of the *trans* double bond (956 cm^{-1}) and the sulfinyl groups (1043 cm^{-1}). At 100 °C all sulfinyl groups which give rise to double bonds have been eliminated, and the intensity of the *trans*-vinylene double bond signal has reached its maximal absorption. During the isothermal stay at 100 °C, neither of these signals changes. In the third part of the heating program (100 to 300 °C), the sulfinyl signal further declines. This second decrease in sulfinyl signal progressed without formation of additional double bonds and thus has to originate from the elimination of the sulfinyl end groups. At 175 °C, both the main-chain sulfinyl groups and the sulfinyl end groups have been eliminated completely from the oligomer.

The selective elimination was further investigated on a sample of precursor oligomer **7** which was converted to the conjugated oligomer **8** by heating a thick precursor film for 3 h at 100 °C under vacuum. The resulting conjugated oligomer **8** still proved to be soluble in common organic solvents. The UV−vis spectrum (in toluene) of this conjugated oligomer shows several maxima at different wavelengths (Figure 10). When the sample was heated further until 270 °C, the sulfinyl end groups were removed and the conjugated oligomers became insoluble. A spectrum of the oligomer **8** in film after heating until 270 °C is also shown in Figure 10.

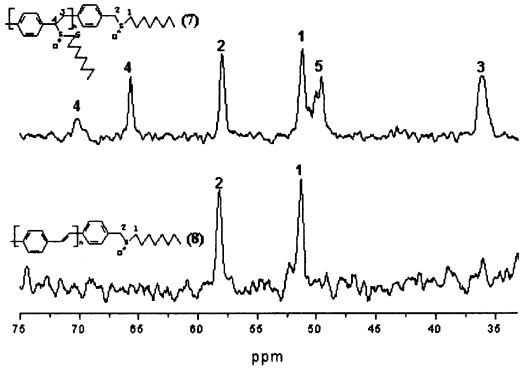


Figure 11. Enlarged part of the ^{13}C NMR spectrum of the sulfinyl precursor oligomer **7** (upper) and the conjugated oligomer **8** (lower).

These maxima probably arise from a distribution in conjugated chain lengths. The first maximum in the UV spectrum of the oligomer at 327 nm corresponds to that of *trans*-stilbene (328 nm). The other maxima at 341, 363, and 390 nm probably correspond to the larger conjugated systems where *n* is 2, 3, and 4, respectively (Figure 10). These wavelengths are in the line of expectation when compared with the wavelengths of PPV oligomers synthesized previously.[25]

The selective elimination was also confirmed by ^{13}C NMR spectroscopy. In the ^{13}C spectrum of the precursor oligomer **7** chemical shifts of several carbon atoms of the main-chain sulfinyl groups slightly differ from those of the sulfinyl end groups. In Figure 11 an enlarged part of the ^{13}C spectrum for both the precursor and the conjugated oligomer is shown. On the precursor stage different signals can be observed which can be assigned to C1 to C5[26] (Figure 11). In the conjugated structure only the two signals for the sulfinyl end groups C1 and C2 remain. All sulfinyl groups in the main chain have been eliminated, and this results in the formation of a new signal in the ^{13}C spectrum at 127 ppm which is attributed to the carbon atoms of the double bond.

These experiments clearly demonstrate that it is kinetically possible to separate elimination of the main-chain sulfinyl groups and thermolysis of the sulfinyl end groups in the oligomer chain. At lower temperatures the sulfinyl groups from the main chain are eliminated, and the double bonds are formed. At higher temperatures thermolysis of the sulfinyl end groups occurs. Furthermore, above 175 °C, we found indications that these sulfinyl end groups were partially converted to carbonyl functionalities or that two oligomer chains may couple, which after oxidation leads to an extension of "effective conjugation length".

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