Identification and Quantification of Polymerization Defects in ^{13}C-Labeled Sulfinyl and Gilch OC_1C_{10}−PPV by NMR Spectroscopy

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ABSTRACT: By using selectively ^{13}C-labeled sulfinyl and Gilch polymers, only noneliminated groups were demonstrated to be present in significant amounts (ca. 6.9%) in the sulfinyl conjugated OC_1C_{10}−PPV. By means of a two-step elimination procedure, this amount could be reduced to a level less than 0.5%. In the Gilch route on the other hand, a tolane−bisbenzyl unit was confirmed to be the main structural defect. Furthermore, noneliminated groups were clearly present. For both polymerization routes no indications for other types of defects such as cross-links or branching, were detected while strong indications for carbonyl type end groups were found. The nature of all "defects" was elucidated by applying liquid 1D and 2D NMR spectroscopy and the amount was calculated based on fully quantitative ^{13}C NMR spectra.

Introduction

Luminescence and conducting properties of poly(1,4-phenylene vinylidene) PPV and its derivatives have been recently investigated by several research groups, especially since the Cambridge group's report[1] on the electroluminescence character of PPV films sandwiched between the indium−tin oxide (ITO) coated glass anode and a metal cathode. Numerous applications involving this class of conjugated polymers include light emitting diodes,[1] thin film transistors,[2] sensors,[3] and photovoltaic devices.[4] In general, these materials are synthesized by precursor routes such as the Wessling,[5] the Gilch,[6] the xanthate,[7] and the sulfinyl[8] routes. In all these precursor routes, the monomer undergoes a base-induced elimination step which leads to the "real monomer", a *p*-quinodimethane system. In the next step, a soluble and processable precursor polymer is formed which finally is eliminated to a conjugated polymer by thermal or chemical treatment.

The synthesis, and as a consequence the microstructure of the resulting polymer chains, is expected to be a key parameter toward the performance of polymers as an active layer in devices as it strongly influences the chain packing and morphology in the final polymer films. Of course, other device characteristics like the electrodes used, device architecture, and fabrication method will also play an important role. A better understanding of the impact of the microstructure will probably lead to new and better defined materials as well as improved applications.

In this study, we focused on poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylidene), abbreviated MDMO−PPV or OC_1C_{10}−PPV. The synthetic route commonly used in industry to obtain this type of polymer is the dehydrohalogenation or Gilch route.[6,9] Over the last years, a new and promising precursor route toward this and other PPV-based polymers, was developed in our laboratory, the so-called sulfinyl route.[8,10] This route is distinguished from the other routes because it starts from an asymmetric monomer, i.e., where the leaving group (Cl) and polarizer group (S(O)R) are different. On the other hand, in the Gilch and most other precursor routes, the polarizer and leaving groups are identical. An open question is still whether this chemical differentiation will have an influence on the polymer microstructure and final device performance. Previous studies[11] already indicated that there was indeed a difference in luminescence efficiency, gelation temperature, and current−voltage characteristics between polymers obtained via the Gilch and sulfinyl routes. This despite the fact that the ^{13}C spectra of unlabeled sulfinyl and Gilch polymers are the same at first glance. Moreover, a recent comparison[12] between state-of-the-art Gilch and sulfinyl synthesized OC_1C_{10}−PPV/PCBM bulk heterojunction solar cells pointed out that a power conversion efficiency η_c of nearly 3% is reached for the sulfinyl based device compared with 2.5% for the Gilch one. This feature of sulfinyl OC_1C_{10}−PPV/PCBM bulk heterojunction solar cells is a consequence of a higher fill factor, incident photon per converted electron value, and short circuit current. This finding can be attributed to a different microstructure resulting from the higher chemical selectivity during polymerization. The microstructure is expected to be responsible for the different device characteristics. Recently, Becker et al.[13] elucidated the microstructure of Gilch-OC_1C_{10}−PPV by introducing ^{13}C labels into the polymer chain. As main structural defects they found the presence of tolane−bisbenzyl moieties. After signal assignment by means of qualitative ^{13}C spectroscopy, they could roughly estimate the amount of the tolane−bisbenzyl moieties from the ^{1}H spectrum as being 1.5−2.2%. They further assumed a similar amount of single bonds (bisbenzyl moiety) and triple bonds (tolane moiety), which means that in total 3−4.4% of the vinylidene bonds were replaced by irregular bonds in the main chain. This approach has inspired us to compare Gilch (Covion procedure[13]) and sulfinyl polymers, but based on more chemical shift selective quantitative ^{13}C NMR spectroscopy. In this way, a deeper insight into the type and amount of structural irregularities in the polymer chain will be obtained. The starting point toward a

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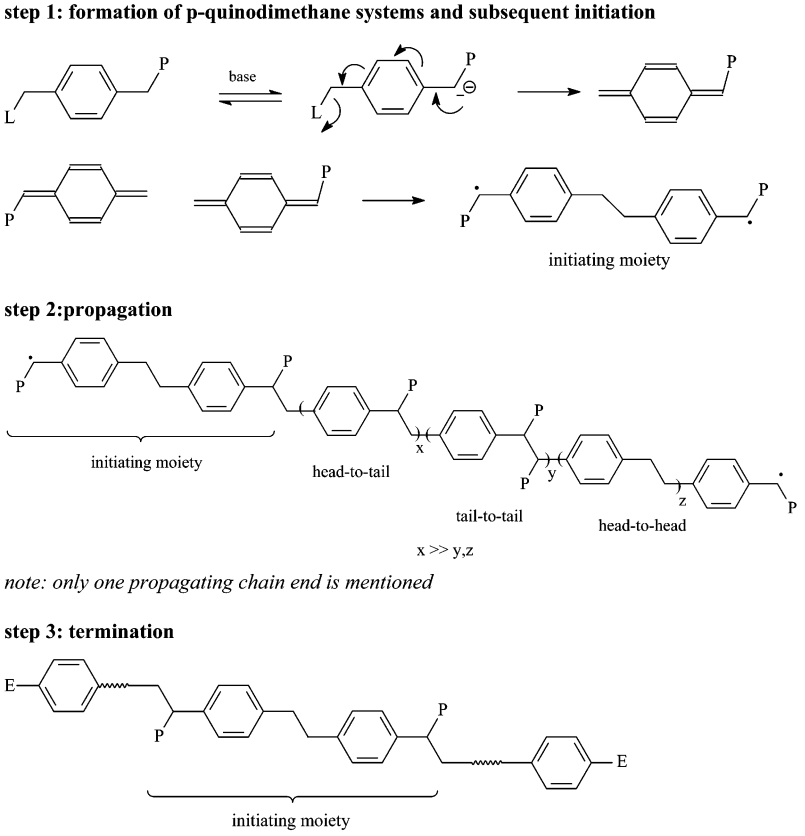
Scheme 1. Radical Precursor Polymerization Mechanism for OC_1C_{10}-PPV[a]



[a] L = Cl. P = Cl (Gilch); P = S(O)R (sulfinyl). E = C(O)H, C(O)OH, $CH_2S(O)R$, or CH_2Cl.

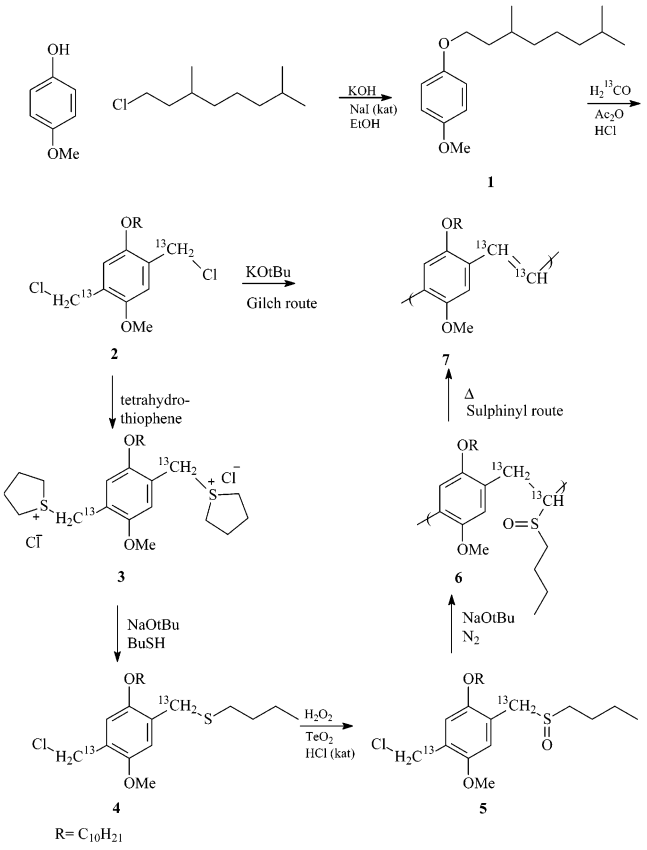
straightforward assignment of these structural defects can be found in the polymerization mechanism of both routes (Scheme 1). The first step—a base-induced 1,6-elimination—leads to the formation of intermediate *p*-quinodimethane moieties. These species are the actual reactive monomers. Next, a free radical polymerization mechanism[14,15] is claimed for the sulfinyl route and strong indications are present that the main Gilch polymerization mechanism, leading to high molecular weight polymers, is also radical in nature.[14] On the other hand, the addition of additives like 4-methoxyphenol[16] and 4-*tert*-butylbenzyl chloride[17] favors the anionic polymerization mechanism leading to low molecular weight polymers. In the radical mechanism, a diradical acts as the initiating moiety (step 1). Both sides of the diradical can propagate (step 2) independently by reaction with *p*-quinodimethane intermediates. One assumes that this mainly happens via a head-to-tail addition, leading to a regular polymer chain. Defects in the "regular" polymer chain such as cross-links, CH_2-CH_2 bond formation (head-to-head addition) in connection with CHS(O)R−CHS(O)R, or CHCl−CHCl bond formation (tail-to-tail addition) can be introduced into this step. Currently, the nature of the termination reaction (step 3) remains undetermined, but two pathways are proposed. Either a hydrogen atom transfer or carbonyl formation by oxygen can take place (see below). Finally, the resulting precursor polymer is converted to the conjugated form. In this study, we were able to identify and quantify structural irregularities present in the corresponding conjugated polymers, by synthesizing the ^{13}C-labeled monomers **(2 + 5)** and corresponding polymers (**7**) (Scheme 2) according to the sulfinyl[18] and Gilch procedures.

Experimental Section

Synthesis of the Labeled Gilch Monomer and Polymers.[13] Synthesis of the Labeled Sulfinyl Monomer and Polymers. Preparation of 1-(3,7-Dimethyloctyloxy)-4-methoxybenzene, 1. In a three-neck round-bottom flask were dissolved 10 g of *p*-methoxyphenol (80.3 mmol), 4.92 g of KOH (87.8 mmol), and 1.2 g of sodium iodide (8.06 mmol) in 34 mL ethanol. During refluxing, 1-chloro-3,7-dimethyloctane (14.9 g, 84.6 mmol) was added dropwise. After being stirred for 62 h, the mixture was cooled, decanted, and extracted with choroform (3 × 200 mL) and 10% NaOH. The organic phases were combined, dried over $MgSO_4$ and evaporated under reduced pressure. A yield of 13.7 g (52%) of **1** was obtained. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.8 (4H, H_{arom}); 3.9 (2H, OCH_2); 3.7 (s, 3H, OCH_3); 1.8(1H); 1.7 (1H); 1.6 (2H); 1.4 (2H); 1.3 (1H); 1.2 (3H); 1.0 (d, J = 6.6 Hz, 3H, CH_3); 0.9 (d, J = 6.7 Hz, 6H; 2 × CH_3). MS (EI, *m*/*z*, relative intensity (%)): 264.

Preparation of 2,5-Bis(chloro-^{13}*C*-methyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene, 2. A 3.26 g (0.012 mol) sample of **1** and 1 g (0.033 mol) of paraformaldehyde-^{13}*C* (isotopic purity of 99%, Cambridge Isotope Laboratory, Inc., Andover) were placed in a 100 mL three-neck round-bottom flask. After addition of 6.5 g (0.066 mol) of 37% HCl under N_2, a 12.25 g (0.12 mol) sample of acetic anhydride was added dropwise at such a rate that the internal temperature did not exceed 70 °C. After being stired for 3.5 h at 75 °C, the mixture was cooled and a light colored solid crystallized at 30 °C. Afterward, the reaction mixture was admixed with 11 mL of cold-saturated sodium acetate solution, followed by a dropwise addition of 25% NaOH (8 mL). The mixture was heated to 52 °C and subsequently cooled in an ice bath while stirring. The cream-colored solid was filtered off, washed with water (7 mL), and dissolved in hexane (24 mL). After extraction with water, the yellowish organic phase was dried over $MgSO_4$, filtered and evaporated. After crystallization, a 3.78 g (87%) of **2** was isolated. By ^{1}H NMR an isotopic purity of 99.2% was determined. Melting point: 65 °C. ^{1}H NMR (300 MHz, $CDCl_3$), δ:

Scheme 2. Preparation of the ^{13}C-Labeled Monomer and OC_1C_{10}−PPV



6.9 (m, 2H, H_{ar}); 4.9 +4.4 (s, 4H, CH_2Cl, ^1J = 152 Hz); 4.0 (m, 2H, OCH_2); 3.8 (s,3 H, OCH_3); 1.9 (1H); 1.7 (1H); 1.6 (2H); 1.4 (2H); 1.3 (1H); 1.2 (3H); 1.0 (d, J = 6.6 Hz, 3H, CH_3); 0.9 (d, J = 6.7 Hz, 6H; 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 19.8 (1C); 22.6 (2C); 24.6 (1C); 27.9 (1C); 30.2 (1C); 36.6 (1C); 37.4 (1C); 39.2 (1C); 41.2 (2C); 56.4 (1C); 67.9 (1C); 113.2 (1C); 114.3 (2C); 127.0 (2C); 151.4(2C). MS(CI, *m*/*z*, relative intensity (%)): 362 $[M + 1]^+$.

Preparation of the Bis(tetrahydrothiophenium) Salt of 2,5-Bis(chloro-^{13}*C*-methyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene, 3. A solution of 3.7 g (0.01 mol) of **2** and 3.7 g (0.04 mol) of tetrahydrothiophene in MeOH (10 mL) was stirred for 70 h at ambient temperature. After precipitation in acetone (100 mL), the precipitate was washed with hexane. The product (4 g, 72%) was dried under reduced pressure at room temperature. ^{1}H NMR (300 MHz, D_2O), δ: 7.1 (d, 2H, H_{ar}); 4.6 + 4.2 (d, 4H, CH_2S, ^1J = 149 Hz); 4.0 (m, 2H, OCH_2); 3.8 (s, 3H, OCH_3); 3.4 (m, 8H, $S(CH_2)_2(CH_2)_2$); 2.2 (m, 8H, $S(CH_2)_2(CH_2)_2$); 1.8 (1H); 1.7 (1H); 1.6 (2H); 1.4 (2H); 1.3 (1H); 1.2 (3H); 1.0 (d, J = 6.6 Hz, 3H, CH_3); 0.9 (d, J = 6.7 Hz, 6H; 2 × CH_3). ^{13}C NMR (100 MHz, D_2O), δ: 21.3 (1C); 24.31/24.39 (2C); 26.4 (1C); 29.6 (1C); 30.7 (1C); 31.3 (1C); 37.6 (1C); 38.7 (1C); 40.9 (1C); 43.9 (2C); 45.5 (1C); 58.6 (1C); 70.0 (1C); 117.8/118.6 (2C); 121.9/122.4 (2C); 153.7/154.3 (2C).

Preparation of 2-(^{13}*C*-Butylsulfanyl)methyl)-5-(^{13}*C*-chloromethyl)-1-(3,7-dimethyloctloxy)-4-methoxybenzene, 4. A mixture of NaO^{t}Bu (0.69 g, 7.18 mmol) and *n*-butanethiol (0.64 g, 7.18 mmol) in MeOH (12 mL) was stirred for 30 min at room temperature. The clear solution was added in one portion to a stirred solution of **3** (4 g, 7.18 mmol). After 1 h, the reaction mixture was neutralized with aqueous HCl, if necessary, and concentrated in vacuo. The crude product was diluted with $CHCl_3$ (21 mL), the precipitate was filtered off, and the solvent was evaporated. The obtained oil was diluted with petroleumether (boiling range 100−140 °C) and concentrated to remove the tetrahydrothiophene. This sequence was repeated three times to afford a light yellow viscous oil. A 2.6 g (6.19 mmol) of crude product was formed. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.89/6.87 (d, 2H, H_{ar}); 4.88/4.87 + 4.37/4.36 (dd, 2H, ^1J = 152 Hz, CH_2Cl); 4.0 (m, 2H, OCH_2); 3.9/3.5 (dd, 2H, ^1J = 144 Hz, $CH_2S(R)$); 2.5 (m, 2H, $SCH_2(CH_2)_2CH_3$); 1.9−1.2 (14H, $H_{alif.}$); 1.0 (3H, CH_3); 0.9 (9H, 3 × CH_3). MS(CI, *m*/*z*, relative intensity (%)): 417 $[M + 1]^+$.

Preparation of 2-(^{13}*C*-Butylsulfinyl)methyl)-5-(^{13}*C*-chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene, 5. An aqueous (35 wt %) solution of H_2O_2 (1.2 g, 12.4 mmol) was added dropwise to a solution of crude thioether **4** (6.19 mmol), TeO_2 (0.12 g, 0.74 mmol), and three drops of concentrated HCl in 1,4-dioxane (24 mL). The reaction was followed on TLC (time: 2.5 h) and as soon as the overoxidation took place, it was quenched by a saturated aqueous NaCl solution (30 mL). After extraction with $CHCl_3$ (3 × 30 mL), the organic layers were dried over $MgSO_4$ and concentrated in vacuo. The reaction mixture was purified by column chromatography (SiO_2, eluent hexane/ethyl acetate 60/40) to give pure **5** (1.74 g, 65%) starting from the tetrahydrothiophenium salt as a light yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.9 (d, 1H, H_{ar}); 6.8 (d, 1H, H_{ar}); 4.8/4.3 (d, 2H, ^1J = 152 Hz, CH_2Cl); 4.3/4.1 + 3.8/3.6 (dd, 2H, ^1J = 130 Hz, $CH_2S(O)R$); 3.9 (m, 2H, OCH_2); 3.8 (s, 3H, OCH_3); 1.9 (1H); 1.7 (1H); 1.6 (2H); 1.4 (2H); 1.3 (1H); 1.2 (3H); 1.0 (d, J = 6.6 Hz, 3H, CH_3); 0.9 (d, J = 6.7 Hz, 6H; 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.5 (1C); 19.8 (1C); 22.1 (1C); 22.6 (2C); 24.6 (2C); 27.9 (1C); 30.2 (1C); 36.6 (1C); 37.4 (1C); 39.2 (1C); 41.3 (1C); 49.7 (1C); 52.5 (1C); 56.4 (1C); 67.9 (1C); 112.8 (1C); 115.7 (1C); 119.7 (1C); 127.0 (1C); 151.4 (2C). MS (CI, *m*/*z*, relative intensity (%)): 433 $[M + 1]^+$.

Preparation of the Precursor Polymer of 2-(^{13}*C*-Butylsulfinyl)methyl-5-(^{13}*C*-chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene, 6, According to the Sulphinyl Route. A solution of 0.5 g of monomer **5** (1.15 mmol) in 2-butanol (8 mL) and a solution of 0.14 g NaO^{t}Bu (1.5 mmol) in 2-butanol (5 mL) was degassed for 1 h at 30 °C by passing through a continuous stream of nitrogen. The base solution was added in one portion to the stirred monomer solution. After 1 h, the reaction mixture was poured dropwise into a well-stirred amount of ice water (115 mL), neutralized with aqueous hydrogen chloride, and extracted with $CHCl_3$ (3 × 50 mL), and the combined organic layers were concentrated in vacuo. A yield of 0.36 g of precursor **6** (77%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.9−6.2 (br m, 2H, H_{ar}); 4.9/4.6 (br d, 1H, Ar-*CH*S(O)R); 4.0−2.9 (br m, 7H, OCH_2, OCH_3, Ar−CHS(O)R−CH_2−Ar); 2.7−2.1 (br d, 2H, −$SCH_2(CH_2)_2CH_3$); 1.9−1.0 (br m, 14H, $H_{aliph.}$); 1.0−0.8 (m, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 151.4 (C_{3+6}, 2C); 127.0 (C_{1+4}, 2C); 110.5 (C_{2+5}, 1C); 67.9 (C_{10}, 1C); 59.1/55.1 (C_8, 1C); 56.4 (C_9, 1C); 39.2 (C_{15}, 1C); 37.4 (C_{13}, 1C); 36.6 (C_{11}, 1C); 32.1/29.1 (C_7, 1C); 30.2 (C_{12}, 1C); 27.9 (C_{16}, 1C); 24.6 (C_{14}, 1C); 22.6 (C_{17}, 2C); 19.8 (C_{18}, 1C); 49.7 ($C_{1'}$, 1C); 24.6 ($C_{2'}$, 1C); 21.9 ($C_{3'}$, 1C); 13.5 ($C_{4'}$, 1C).

Thermal Conversion of Precursor Polymer to Conjugated Polymer 7. A solution of **6** (0.35 g) in toluene (22 mL) was degassed for 1 h by passing through a continuous stream of nitrogen. The solution was heated to 110 °C and stirred for 3 h. After cooling to 50 °C, the resulting orange-red solution was precipitated dropwise in methanol in a ratio toluene/methanol 1/10. The polymer was filtered off, washed with methanol and dried at room temperature under reduced pressure. The polymer was purified by dissolving it in 25 mL of THF (68 °C), cooling the solution to 40 °C, and precipitating dropwise in methanol (45 mL). A 0.2 g (0.69 mmol, 77%) of **7** was obtained as a red, fibrous polymer. ^{1}H NMR (400 MHz, C_2 D_2Cl_4), δ: 7.5 (br, 2H, $H_{olef.}$); 7.2 (br, 2H, H_{ar}); 5.2 (d weak, ^1J = 134 Hz, Ar−*CH*S(O)R−CH_2−Ar); 4.6−3.2 (br m, 5H, OCH_2, OCH_3 + (3.7 ppm, Ar−CHS(O)R−CH_2−Ar)); 2.1−0.6 (br m; 19H; $H_{aliph.}$). ^{13}C NMR (100 MHz, $CDCl_3$): 151.4 (C_{3+6}, 2C); 127.0 (C_{1+4}, 2C), 123.3 (C_{7+8}, 2C); 110.5 (C_2, 1C); 108.8 (C_5, 1C); 67.9 (C_{10}, 1C); 56.4 (C_9, 1C); 39.2 (C_{15}, 1C); 37.4 (C_{13}, 1C); 36.6 (C_{11}, 1C); 30.2 (C_{12}, 1C); 27.9 (C_{16}, 1C); 24.6 (C_{14}, 1C); 22.6 (C_{17}, 2C); 19.8 (C_{18}, 1C). (2.7 g, 7.75 mmol, 78%). Molecular weight determination by SEC in THF against polystyrene standards gave M_w = 426 000 g/mol and a polydispersity of 4.7. The unlabeled polymer was prepared analogously.

Synthesis of Model Compounds. Preparation of 1,4-Bis(butylsulfanyl)benzene, 8. A mixture of *n*-butanethiol (12 g, 0.14 mol) and NaO^{t}BuO (13.1 g, 0.14 mol) was dissolved in methanol/THF (1/3) and in one portion added to a stirred solution of 6 g (0.034 mol) of dichloro-*p*-xylene in THF (30 mL). The mixture was heated to reflux, and after 2 h the reaction was finished. The mixture was cooled to room temperature. The salts were filtered off and the liquid was concentrated in vacuo. A 9.6 g sample of 1,4-bis(butylsulfanyl)benzene (0.03 mol, 98%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.2 (s, 4H, H_{ar}); 3.6 (s, 4H, Ar−CH_2−SR); 2.4 (t, 4H, Ar−CH_2−S−CH_2−$(CH_2)_2CH_3$); 1.5 (m, 4H, −S−CH_2−CH_2-CH_2−CH_3); 1.3 (m, 4H, −S−CH_2−CH_2−CH_2−CH_3); 0.9 (m, 6H; 2 × CH_3). MS (EI, *m*/*z*, relative intensity (%)): 250.

Preparation of 1,4-Bis(butylsulfinyl)benzene, 9. An aqueous (35 wt %) solution of H_2O_2 (8.5 g, 0.085 mol) was added dropwise to a solution of 0.4 g 1,4-bis(butylsulfanyl)-benzene, TeO_2 (1.3 g; 8 mmol), and three drops of concentrated HCl in 128 mL of 1,4-dioxane. The reaction was followed on TLC (19/1 dichloromethane/methanol), and as soon as the overoxidation took place, the reaction was quenched by a saturated aqueous NaCl solution (150 mL). The reaction mixture was extracted with $CHCl_3$ (3 × 200 mL), the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The reaction mixture was purified by column chromatography (SiO_2, eluent dichloromethane/methanol 19/1) to give pure 1,4-bis(butylsulfinyl)benzene (6.3 g, 0.02 mol, 60%) which appears as white crystals after evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.3 (s, 4H, H_{ar}); 3.9 (s, 4H, Ar−CH_2−SR); 2.5 (t, 4H, Ar−CH_2−S−CH_2−$(CH_2)_2CH_3$); 1.7 (m, 4H, −S−CH_2−CH_2-CH_2−CH_3); 1.4 (m, 4H, −S−CH_2−CH_2−CH_2−CH_3); 0.9 (m, 6H; 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.5 (2C); 21.9(2C); 24.6 (2C); 49.7 (1C); 57.6 (1C); 130.5 (1C); 137.8 (1C); 128.7 (2C); 129.0 (2C). MS (EI, *m*/*z*, relative intensity (%)): 282. T_m = 192 °C.

Preparation of 1,4-Bis(butylsulfinyl)-4′-chlorobenzene, 10. A 1.3 g sample of *N*-chlorosuccinimide (0.01 mol) was added portionwise as a solid to a solution of 3 g of 1,4-bis(butylsulfinyl)benzene (0.01 mol) in 50 mL of dichoromethane (time: 30 min). The solution was stirred at room temperature. The mixture was extracted with water (3 × 50 mL) and dried over $MgSO_4$. After column chromatography (SiO_2, chloroform/methanol 19/1) the product could be isolated as white crystals (2.7 g, 7.75 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.5 (m, 2H, H_{ar}); 7.4 (m, 2H, H_{ar}); 5.54 (d, 1H, CHClS(O)R); 4.0 (s,2H, CH_2S(O)R); 2.6 (m, 2H, $S(O)CH_2(CH_2)_2CH_3$); 2.4 (m, 2H, $S(O)CH_2(CH_2)_2CH_3$); 1.7 (m, 2H, S(O)$CH_2CH_2CH_2CH_3$), 1.4 (m, 2H, S(O)CH2−CH2CH2CH3); 0.9 (m, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.5 (2C); 21.9 (2C); 24.6 (2C); 49.7 (1C); 51.1 (1C); 57.6 (1C); 74.7−73.1 (1C); 130.5 (1C); 137.8 (1C); 128.6 (2C); 129.0 (2C). MS (CI, *m*/*z*, relative intensity (%)): 349 $[M + 1]^+$. T_m = 143 °C.

Preparation of Poly(*p*-Phenylene-1,2-bis(butylsulfinyl)ethylene) According to the Sulphinyl Route, 11. A solution of 0.4 g of monomer **10** (1.15 mmol) in THF (9 mL) and a solution of NaO^{t}Bu (0.14 g, 1.5 mmol) in THF (5 mL) were degassed for 1 h at 40 °C by passing through a continuous stream of nitrogen. The base solution was added in one portion to the stirred monomer solution. After 1 h, the reaction mixture was poured dropwise in a well-stirred amount of ice−water (150 mL). The mixture was neutralized with aqueous hydrdogen chloride and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were concentrated in vacuo. The obtained polymer was purified by precipitating it in an ice-cold mixture of hexane/diethyl ether 1/1. A 0.15 g of yellow, viscous polymer (0.48 mmol, 40%) was isolated and dried under reduced pressure at ambient temperature.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.5−7.1 (br m, 4H, H_{ar}); 3.9/3.7 (br m, 2H, Ar−*CH*S(O)R−*CH*S(O)R−Ar); 2.7/2.5 (br m, 4H, $S(O)CH_2(CH_2)_2CH_3$); 1.7 (br m, 4H, S(O)$CH_2CH_2CHCH_3$); 1.4 (br m, 4H, S(O)$CH_2CH_2CH_2CH_3$); 0.9/0.8 (b, 6H, CH_3). ^{13}C NMR (400 MHz, acetone-*d*), δ: 14.1 (2C, C_{10}); 22.6 (2C, C_9); 25.2 (2C, C_8); 50.9/51.5 (2C, C_{5+6}); 51.9 (2C, C7); 58.3 (C_{11}); 130−138 (6C, C_{1-4}). M_w = 1592; polydispersity = 1.5.

Analytical Data. NMR Measurements. ^{1}H spectra of the monomers and conjugated polymers were acquired in a dedicated 5 mm probe on a Varian Inova 400 MHz (9.4 T) spectrometer in $CDCl_3$ and $C_2D_2Cl_4$ respectively. The ^{13}C spectra were obtained at 100 MHz with a dedicated carbon 10 mm probe at 40 °C. Typical acquisition parameters are as follows: a spectral width of 21 344 Hz, a filter bandwidth equal to the spectral width, a pulse width of 13 μs, an acquisition time of 0.7 s, and a processing line broadening of 7.5 Hz. For both monomers and polymers, a solution of 46.5 mg in 3.5 mL of $CDCl_3$, containing 30 mg (25 mM) of chromium(III) acetylacetonate to reduce the T_{1C} decay times, was used. According to this procedure, a pulse preparation delay of only 5 s needs to be maintained between consecutive pulses in order to obtain fully quantitative results. Inversed gated decoupling was used to avoid unequal NOE's. ^{1}H and ^{13}C chemical shifts were referenced relative to tetramethylsilane. For proton NMR, both standard 1D and 2D COSY spectra[19] were performed. For carbon NMR, fully quantitative 1D spectra, APT[20] (attached proton test) and DEPT[21] (distortionless enhancement by polarization transfer) spectra were used. Carbon−proton 2D-heteronuclear correlation spectra, HETCOR,[22] were recorded using an evolution time corresponding to an average direct coupling $^1J_{CH}$ value of 140 Hz.

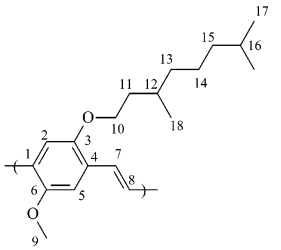
Other Measurements. Molecular weights and molecular weight distributions were determined relative to polystyrene standards with a narrow polydispersity (Polymer Labs) by size exclusion chromatography (SEC). Separation to hydrodynamic volume was obtained using light-scattering experiments on a Spectra Series P100 (Spectra Physics) equipped with two mixed-B columns (10 μm, 2 × 30 cm × 7.5 mm, Polymer Labs) and a refractive index detector (Shodex) at 40 °C. SEC samples were filtered through a 45 μm filter. HPLC grade THF (p.a.) was used as the eluent at a constant flow of 1.0 mL/min. Toluene is used as flow rate marker. Only for product **11** did a different GPC column (5 μm, 100 Å, 300 × 7.5 mm) have to be used.

Direct insertion probe mass spectroscopy (DIP−MS) analyses were carried out on a Finnigan TSQ 70. Either chemical ionization with isobutane as reagent gas, mass range 90−600, and heated at 120 °C/min from 30 to 650 °C or electron impact mode, mass range 35−350, and an inter scan time of 2 s was applied. The electron energy was 70 eV.

Results and Discussion

(a) Optimalization of the NMR Protocol. To obtain the nature and amount of structural defects from a ^{13}C NMR spectrum, fully quantitative NMR spectra are a prerequisite. In this way, our approach is different from the one of Becker et al.,[13] since they estimated the amount of defects from the less chemical shift selective ^{1}H NMR spectra. Another drawback of ^{1}H NMR is that several functionalities, e.g., internal triple bonds and carbonyl groups, are not observed and their quantification is not possible. To acquire quantitative ^{13}C spectra, a preparation delay of five times the longest T_1 relaxation decay time has to be maintained between consecutive pulses in order to let the magnetization return to equilibrium. Therefore, the T_1 decay times of all carbon resonances were determined by means of the inversion recovery technique (Table 1). Since the longest T_1 decay times are on the order of 2.7 s, a preparation delay of at least 13.5 s is required (total experiment time of 21 h for 4300 repetitions). The influence of the paramagnetic relaxation agent chromium(III) acetylacetonate on the T_1 relaxation decay times was examined. The addition of chromium(III) acetylacetonate however has to be made cautiously since too high concentrations can reduce the T_2 decay time significantly (increased line width). Therefore, the effect of varying concentrations of chromium(III) acetylacetonate on the T_1 relaxation

Table 1. Chemical Shift Assignments of the Carbon Atoms of OC_1C_{10}−PPV in $CDCl_3$ and T_1 Relaxation Decay Times as a Function of the Concentration of Chromium(III) Acetylacetonate



		T_1 (s)		
carbon atom	δ (ppm)	native	20 mM Cr (III)	25 mM Cr(III)
3 + 6	151.4	2.40	0.90	0.76
4 + 1	127.0	1.89	1.00	0.53
7 + 8	123.3	0.38		0.16
2 + 5	110.5	0.12	0.10	0.23
10	67.9		0.35	0.29
9	56.4	0.93	0.31	0.30
15	39.2	1.10	0.77	0.67
13	37.4	0.44	0.41	0.37
11	36.6	0.35	0.24	0.30
12	30.2	0.75	0.60	0.44
16	27.9	2.68	1.30	1.02
14	24.6	0.75	0.54	0.52
17	22.6	1.67	1.03	0.79
18	19.8	0.82	0.57	0.49

decays was evaluated. Table 1 shows that the longest T_1 relaxation decay in the presence of 30 mg of chromium(III) acetylacetonate (25 mM) is 1.0 s, allowing acquisitional quantitative data with a preparation delay of 5.0 s (total experiment time 7 h for 4300 scans). Moreover, NOE effects (which were significantly reduced by inverse gated decoupling) are further suppressed by chromium(III) acetylacetonate. Paramagnetic relaxation agents mainly provide an additional relaxation mechanism that suppresses the C−H dipole−dipole relaxation responsible for the NOE enhancement.[23] An increase of the filter bandwidth equal to the spectral width was also applied to improve quantification of the peaks at the edges of the spectrum.

(b) Study of the Structural Defects Present in the Polymers Obtained via the Gilch Route. By comparing the ^{13}C NMR spectra of the unlabeled (Figure 1a) and labeled (Figure 1b) eliminated conjugated polymers, it is obvious that some additional resonances can be detected upon labeling. These resonances are situated at 31.0, 33.6, 38.3, 58.6, 90.4, 165.2, and 188.9 ppm. While the resonances at 31.0, 90.4, 165.2, and 188.9 ppm were also observed by Becker et al.,[13] some new resonances appear in our spectra. All of these signals are broadened due to the scalar $^1J_{CC}$ coupling and because they arise from carbons of the polymer backbone. The resonances mentioned above were not detected in the spectrum of the unlabeled polymer, indicating that they are present in an amount less than 10%. The very intense resonance signal at 123.2 ppm originates from the ^{13}C-labeled double bond atoms of the conjugated backbone. The corresponding proton lines (7.7 and 7.3 ppm) were assigned by means of one-bond HETCOR spectra and appear as doublets in the proton spectra with a typical $^1J_{CH}$ value of 151 Hz. To calculate the amount of structural defects from the ^{13}C NMR spectra, the summed integration of some signals (carbon atom 3, 6, 17 and 18) was taken as an internal reference to which the other resonances were normalized. For

Table 2. Overview of the Type and Amount of the Structural Defects Present in the Gilch Polymer

δ (ppm)	structural defect	amount (%)
31.0	bisbenzyl	5.6
33.6/38.3	noneliminated groups	1.8
90.4	triple bond	4.2
129.0	chloro−vinyl	∼1.4
165.2	carboxylic acid	∼0.2
188.9	aldehyde	∼0.1

spectral regions containing both defect and regular signals, reduction of the total intensity with the intensity of the regular signals (based on the normalized integrals) allows quantification of the structural defects.

The main structural defects are clearly represented by the signal of the triple bond (90.4 ppm), which is a product of a tail-to-tail addition, as well by the signal of the bisbenzyl unit (31.0 ppm), which originates from a head-to-head addition (cf. Scheme 1). By means of DEPT, the resonances at 31.0 and 90.4 ppm were shown to arise from a methylene carbon and a quaternary carbon atom, respectively. By applying the proposed procedure, it was found that the tolane moiety (triple bond) appears in an amount of 4.2%, while the bisbenzyl unit (single bond) was present for 5.6%. In Table 2, the assignments of the structural defects and their fractions are reported. The higher defect level of the bisbenzyl unit as compared to the tolane unit, will be explained later.

By DEPT, the resonances at 33.6 and 38.3 ppm were assigned to a methylene and a methine carbon atom, respectively. These resonances are present in equal amounts (1.8%) and are attributed to the noneliminated groups (−CH_2−CHCl−). We remark that this defect was not observed in the ^{13}C NMR spectrum of the polymer synthesized by Becker et al.[13] recorded in $C_2D_2Cl_4$ at 90 °C. Therefore, a ^{13}C NMR spectrum of our Gilch polymer was acquired under the same experimental conditions ($C_2D_2Cl_4$, 90 °C, and a pulse preparation delay of 15 s since no chromium(III) acetylacetonate was used to reduce the T_{1C} decay times). Under these conditions, the resonances in question appear more broadend and are clearly more difficult to detect (Figure 1b—expanded region, top). Note that it took about 80 h to acquire this high *S*/*N* spectrum. An explanation why Becker et al. did not observe these resonances can most probably be found in the experimental conditions used and the much weaker *S*/*N* ratio of their spectra.

It is further assumed that the peak at 129.0 ppm arises from a successor of the tail-to-tail addition namely the chloro−vinyl bond. Although it is impossible to determine the exact amount due to overlap with the signals of the aromatic and olefinic carbons, it looks fair to state that the amount covers the difference in amount between tolane and bisbenzyl units (∼1.4%). This implies that, according to our procedure, based on fully quantitative ^{13}C spectra, 11.2% of the vinylidene bonds in Gilch OC_1C_{10}−PPV are replaced by tolane−bisbenzyl moieties. This result is in disagreement with Becker's.[13] Using ^{1}H NMR as determination method, they found 10−12% and 3−4.4% of tolane−bisbenzyl moieties in poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylidene) (MEH−PPV)[24] and OC_1C_{10}−PPV, respectively.

The signals at 188.9 and 165.2 ppm were attributed to aldehyde and carboxylic functionalities present at a level of 0.1 and 0.2%, respectively. Until now, their origin is not clear, but since OC_1C_{10}−PPV is stable up

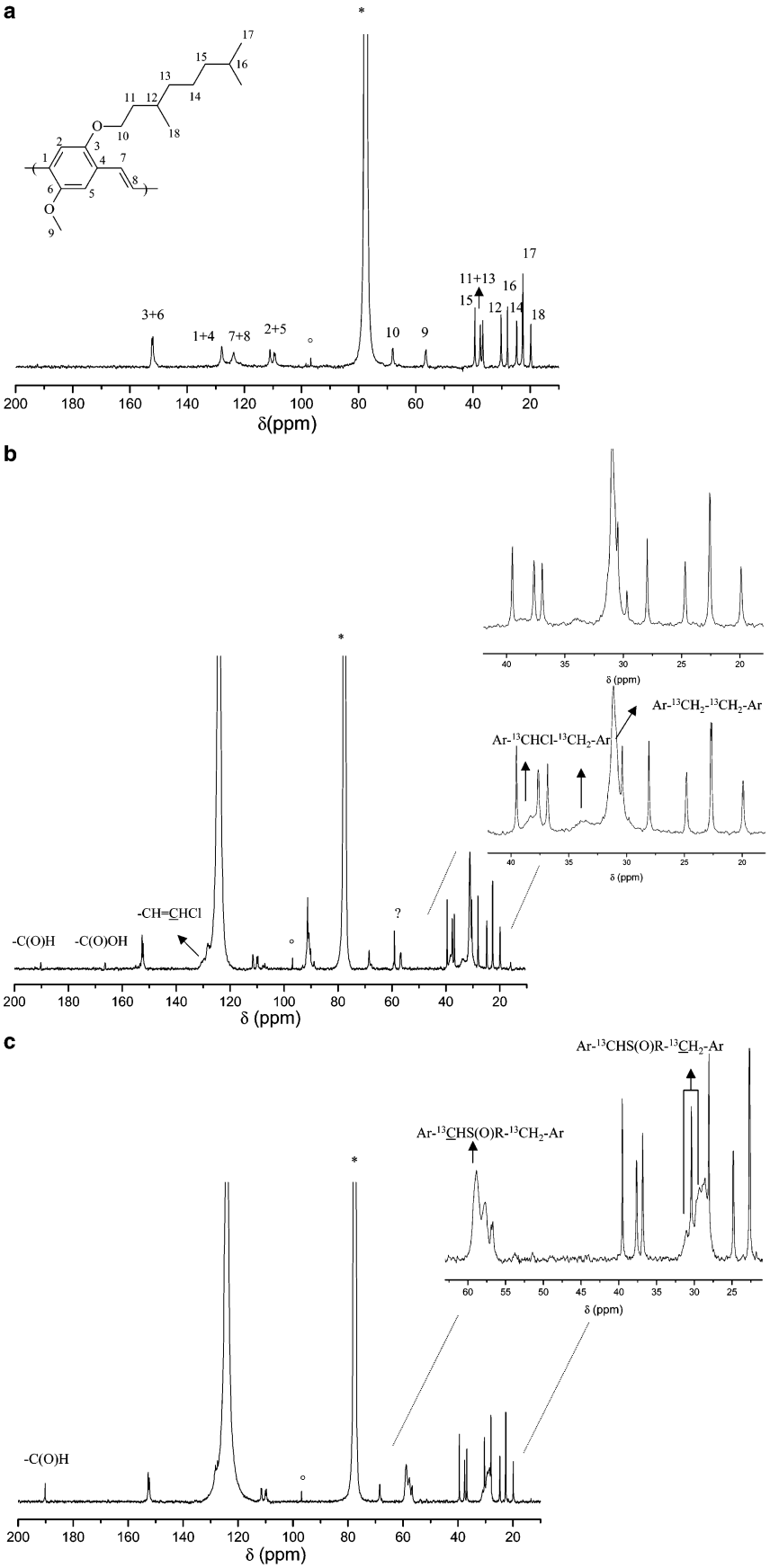


Figure 1. (a) ^{13}C NMR spectrum of unlabeled sulphinyl and Gilch conjugated OC_1C_{10}−PPV at 40 °C. ^{13}C NMR (100 MHz, $CDCl_3$), δ: 151.4 (C_{3+6}, 2C); 127.0 (C_{1+4}, 2C), 123.3 (C_{7+8}, 2C); 110.5 (C_2, 1C); 108.8 (C_5, 1C); 67.9 (C_{10}, 1C); 56.4 (C_9, 1C); 39.2 (C_{15}, 1C); 37.4 (C_{13}, 1C); 36.6 (C_{11}, 1C); 30.2 (C_{12}, 1C); 27.9 (C_{16}, 1C); 24.6 (C_{14}, 1C); 22.6 (C_{17}, 2C); 19.8 (C_{18}, 1C). (b) ^{13}C NMR spectrum of 100% ^{13}C-labeled Gilch OC_1C_{10}−PPV at 40 °C. Expanded region: (bottom) ^{13}C NMR spectrum recorded in $CDCl_3$ at 40 °C; (top) ^{13}C NMR spectrum recorded in $C_2D_2Cl_4$ at 90 °C. (c) ^{13}C NMR spectrum of 100% ^{13}C-labeled sulfinyl OC_1C_{10}−PPV at 40 °C. The resonances marked with an asterisk and an open circle result from $CDCl_3$ and the transmitter offset, respectively.

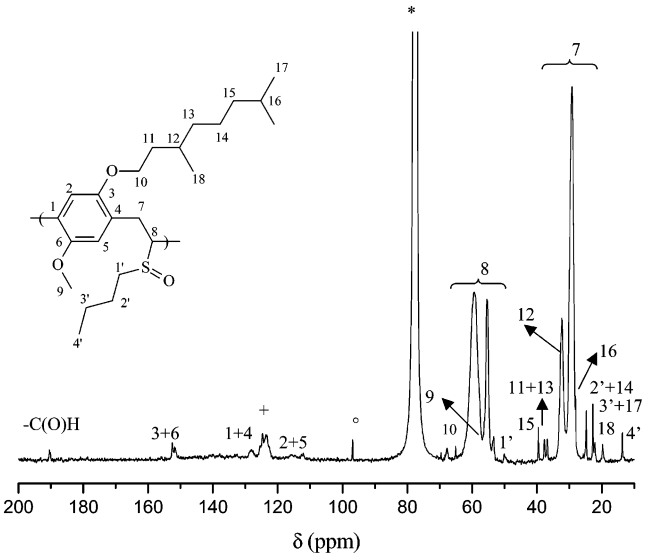


Figure 2. ^{13}C NMR spectra of 100% ^{13}C-labeled sulphinyl precursor polymer at 40 °C. The resonances marked with an asterisk and an open circle result from $CDCl_3$ and the transmitter offset, respectively. The resonance marked with + is due to initial elimination. ^{13}C NMR (100 MHz, $CDCl_3$), δ: 151.4 (C_{3+6}, 2C); 127.0 (C_{1+4}, 2C); 110.5 (C_{2+5}, 1C); 67.9 (C_{10}, 1C); 59.1−55.1 (C_8, 1C); 56.4 (C_9, 1C); 39.2 (C_{15}, 1C); 37.4 (C_{13}, 1C); 36.6 (C_{11}, 1C); 32.1−29.1 (C_7, 1C); 30.2 (C_{12}, 1C); 27.9 (C_{16}, 1C); 24.6 (C_{14}, 1C); 22.6 (C_{17}, 2C); 19.8 (C_{18}, 1C); 49.7 ($C_{1'}$, 1C); 24.6 ($C_{2'}$, 1C); 21.9 ($C_{3'}$, 1C); 13.5 ($C_{4'}$, 1C).

to about 175 °C,[25] they probably are related to the end groups of the polymer as mentioned before. So far, no reasonable explanation for the peak at 58.6 ppm can be offered.

(c) Study of the Structural Defects Present in the Polymer Obtained via the Sulfinyl Route. With respect to the unlabeled eliminated polymer (Figure 1a), new resonances appear around 29.0 and 31.0 ppm, around 57.3 and 58.4 ppm, and at 188.9 ppm (Figure 1c) for the sulfinyl polymer. A combination of APT and DEPT measurements reveals the nature of the two resonances around 57.3 and 58.4 ppm as being methine carbons, while those at 31.0 and 29.0 ppm can be attributed to methylene carbons.

Starting from the resonances at 58.4 and 57.3 ppm and at 31.0 and 29.0 ppm, a comparison of the carbon spectrum of the precursor (Figure 2) and conjugated polymer (Figure 1c) indicates that the two groups of signals are related and represent the noneliminated groups (CH_2−CHS(O)R). The carbon spectrum of the precursor polymer clearly shows both groups of resonances assigned to the carbons 7 and 8 in Figure 2. The presence of the asymmetric carbon atom 8 in combination with the asymmetric sulfoxide group results in four diastereomers of which two pairs, *RR* and *SS* on one hand and *RS* and *SR* on the other hand, can be differentiated by NMR.[26] The splitting of the carbon 8 (58.4 and 57.3 ppm) represents the population distribution of these two pairs of isomers and explains the resultant splitting of the carbon 7 resonance (31.0 and 29.0 ppm) in equal (integration) parts. The correspond-

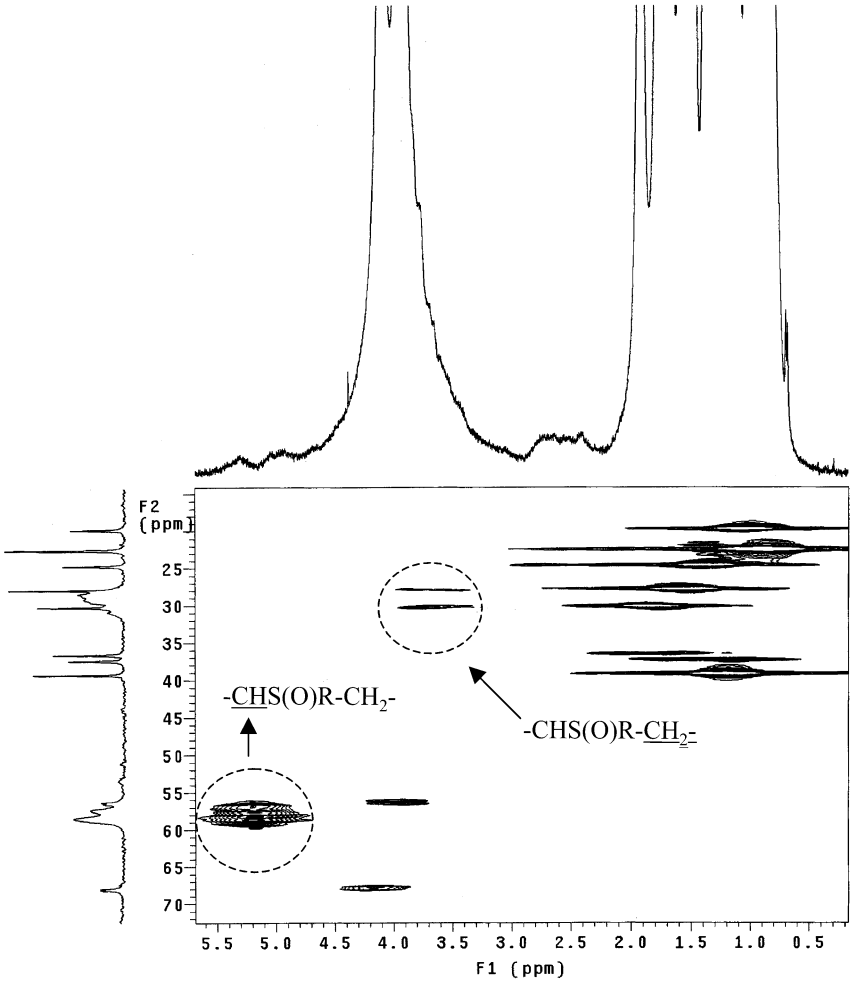


Figure 3. One-bond optimized HETCOR spectrum of ^{13}C-labeled OC_1C_{10}−PPV 40 °C.

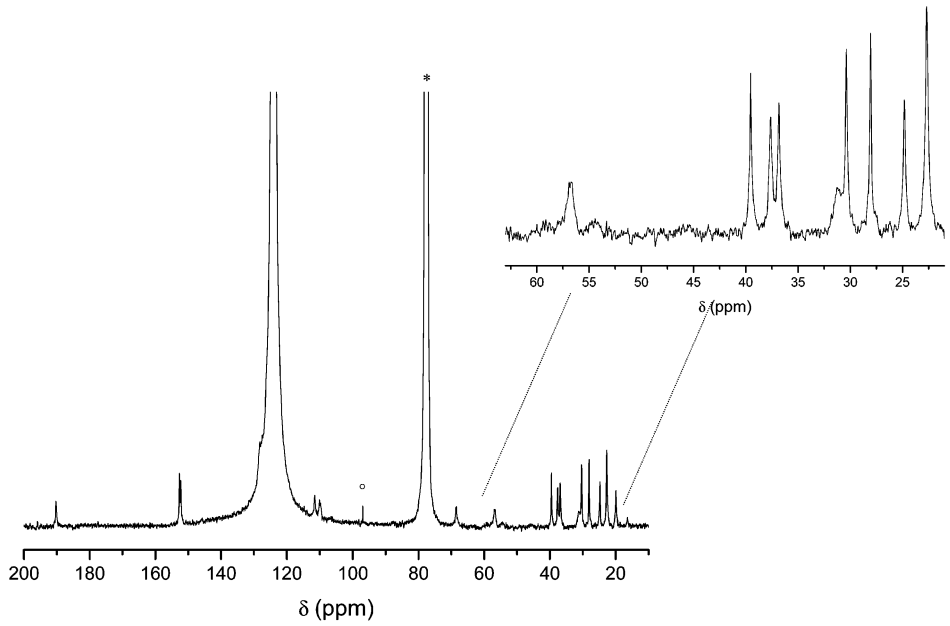


Figure 4. ^{13}C NMR spectrum of 100% ^{13}C-labeled sulfinyl OC_1C_{10}−PPV prepared by the two-step elimination procedure at 40 °C. The resonances marked with an asterisk and an open circle result from $CDCl_3$ and the transmitter offset, respectively.

ing proton resonances were assigned by means of an one-bond optimized HETCOR experiment on the eliminated polymer (Figure 3), which shows that the resonances of carbon atom 8 are correlated with a proton signal around 5.2 ppm, while the resonances of carbon 7 are correlated with a proton resonance around 3.7 ppm. These protons manifest themselves as doublets with a $^1J_{CH}$ value of 134 Hz due to the coupling with the labeled carbons. It should be noted, no correlation was found between the proton resonance at 2.6 ppm and a ^{13}C resonance because the corresponding carbon atom is not labeled. This resonance arises from methylene protons of the noneliminated sulfoxide groups i.e., $-S(O)CH_2-(CH_2)_2CH_3$. After the thermal elimination, one can clearly observe a dramatic decrease of the intensity of both carbon resonances 7 and 8 (compare Figure 2 with Figure 1c). By this, we have proven that the sulfinyl polymer is free from structural defects due to head-to-head and tail-to-tail additions but is characterized by an uncomplete elimination. According to the standard elimination procedure used, i.e., 3 h refluxing in toluene at 110 °C, 6.9% of noneliminated groups remain. These noneliminated groups will act as sp^3-defects, and definitely will disrupt the conjugation of the backbone p orbitals. Since polymer chain organization is without doubt coupled to the mechanical and electrooptical properties, these defects probably will also influence the final performance in the devices.[11,12] To reduce the amount of noneliminated groups further, both the elimination time and temperature were investigated in more detail. By prolonging the elimination time from 3 to 7 h, the amount of noneliminated groups could be further reduced to 2.0%. To increase the elimination temperature the solvent had to be changed from toluene to dichlorobenzene (boiling point 170 °C). This increase in reaction temperature resulted in a reduction in the noneliminated groups to 2.4%. A solution to shift the equilibrium further in the direction of the elimination products in toluene at 110 °C was found in a two-step elimination procedure. After the first elimination step, performed during a 3 h reaction time, the polymer was precipitated and then refluxed in fresh toluene for another 4 h (second elimination). This so-called two-step elimination procedure gave rise to a regio regular OC_1C_{10} polymer with less than 0.5% of noneliminated groups (Figure 4). Also note the small resonance at 31.0 ppm which is supposed to be the initiating moiety since no degradation occurs at 110 °C. The ^{13}C labels reveal resonances from this initiaiting moiety, which normally cannot be detected since the amount present in the polymer chain is too low.

Scheme 3. Preparation of a Tail-to-Tail Model Compound

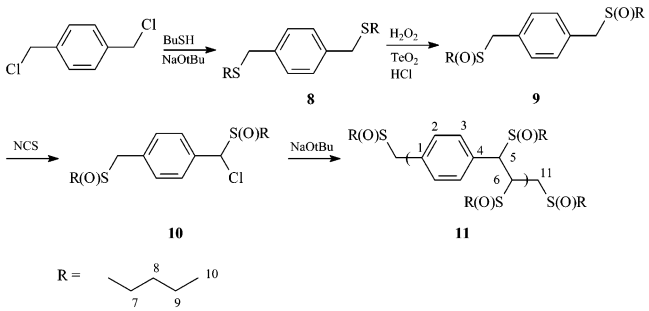


Table 3. Overview of the Type and Amount of the Structural Defects Present in the SulfInyl Polymer

δ (ppm)	structural defect	amount (%)
32.0−29.0 and 58.4−57.3	noneliminated groups	6.9
188.9	aldehyde	∼0.3

The most notable distinction between the sulfinyl and Gilch polymers is the absence of the regio irregularities in sulfinyl-OC_1C_{10}−PPV. This is supported by comparing the ^{13}C chemical shifts of a tail-to-tail addition model compound **11** (Scheme 3 and Experimental Section). Since only oligomers were formed due to steric hindrance of the two sulfoxide groups, we were able to observe the end group resonances ($-CH_2S(O)R$). If we take the influence of electron donating substituents on the aromatic system of OC_1C_{10}−PPV into account,[10] the complete absence of signals in the region between 52 and 40 ppm for the sulfinyl polymer is a strong confirmation that in the sulfinyl route no tail-to-tail additions occur.

Table 4. Influence of Oxygen on the Polymerization and Elimination (3 h in toluene at 110 °C) Reactions of OC_1C_{10}−PPV

sample	polymerization atmosphere	yield of precursor (%)	elimination atmosphere	yield (%)	M_w[a]	M_n[a]	DP[a]
1	N_2	70	N_2	89	560 000	118 000	4.7
2	N_2	61	N_2	80	551 000	244 000	2.3
3	N_2	78	N_2	85	465 000	204 000	2.3
4	N_2	65	N_2	90	560 000	109 000	5.1
5	O_2	16	O_2	81	163 000	32 000	5.0
6	O_2	20	O_2	87	172 000	33 000	5.2

[a] For the eliminated polymer.

Concerning the carbonyl resonances, it must be noticed that the Gilch polymer has two carbonyl functionalities, an aldehyde resonance at 188.9 ppm and a carboxylic acid resonance at 165.2 ppm, while the sulfinyl polymer has only one carbonyl resonance at 188.9 ppm. The latter is present in an amount of 0.3%. Although it is generally suggested that carbonyl groups are most likely related to degradation of the conjugated polymer chain in the presence of oxygen or heat, strong indications were found that they represent the polymer end groups, at least for those prepared by the sulfinyl route. This since the aldehyde resonance is already observed in the spectrum of ^{13}C-labeled sulfinyl precursor polymer (Figure 2): the intensity ratio of the quaternary carbons 3 and 6 to the aldehyde functionality was found to be identical for both the precursor and eliminated polymer (compare Figures 1c and 2). It is assumed that it originates from the reaction between oxygen and the radical ends of the polymer chain. This leads to the formation of a hydroperoxide, which by rearrangement can be converted to an aldehyde group. If so, then oxygen acts as a radical scavenger and subsequently terminates the growing polymer chain (Scheme 2, step 3). Hence, by polymerizing the unlabeled monomer in an oxygen atmosphere (both monomer and base solution were flushed with oxygen at 30 °C instead of nitrogen), we expected a decrease in the molecular weight of the polymers as well as the appearance of aldehyde resonances in the ^{1}H spectrum. As expected, a decrease of the molecular weight as well as a reduction of the yield of the precursor polymer was observed (Table 4). While no aldehyde functions could be detected in the ^{1}H NMR spectrum of the polymer fraction because the molecuar weights are still too high, the ^{1}H spectrum of the residual fraction, which mainly consists of monomer and oligomers, clearly shows the resonances of an aldehyde functionality at 10.2 ppm. This experiment confirms that oxygen terminates a significant part of the growing oligomers, although a small fraction of polymer is still formed.

In Table 3, an overview of the type and amount of the structural irregularities associated with the sulfinyl route is given.

Conclusions

The aim of this study was to examine the nature and amount of the structural irregularities in OC_1C_{10}−PPV obtained by two different precursor routes, namely the Gilch and the sulfinyl route, to clarify the role of the synthesis in their introduction. Gilch and sulfinyl polymers were therefore selectively ^{13}C-labeled in the main chain and examined by liquid state 1D and 2D NMR techniques. The amount of structural "defects" was derived from quantitative ^{13}C NMR spectra. A tolane−bisbenzyl unit (11.2%) was found to be the major defect in eliminated Gilch polymers. Also the presence of noneliminated locations (1.8%) as well as chloro−vinyl bonds (ca. 1.4%), which is a product of the tail-to-tail addition, was demonstrated. In contrast, only a considerable amount of noneliminated groups was found in the conjugated sulfinyl polymers. The amount of noneliminated groups could be reduced by increasing the elimination time (2.0%) or temperature (2.4%). However, a two-step elimination procedure was shown to be the most efficient and results in less than 0.5% of noneliminated groups. Strong indications were further presented to assign the observed aldehyde functionalities to the end groups: oxygen clearly affects the termination reaction of the growing oligomers. In general, we can conclude that in contrast to the Gilch route the polymerization reaction via the sulfinyl route is characterized by a very regular propagation step, most probably due to the different chemistry used in both routes.

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