New Insights into the Microstructure of GILCH-Polymerized PPVs

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ABSTRACT: The microstructure of GILCH-polymerized PPVs was examined by NMR techniques. Selectively main-chain ^{13}C-labeled polymers were prepared and investigated by ^{1}H NMR, ^{13}C NMR, and 2D NMR methods. Only one major polymerization defect was discovered: tolane−bisbenzyl (TBB) moieties could be proven in amounts of 1.5−2.2% for OC_1C_{10}−PPV. Furthermore, indications for ether-type end groups (∼0.2%) were found. These defects are readily explained by the polymerization mechanism. Other structural elements (e.g., cis double bonds, branching) were not detected.

Introduction

Poly(*p*-phenylenevinylene)s (PPVs) are known to be very interesting materials for optoelectronic applications, such as polymer light-emitting diodes (PLEDs)[1] or plastic solar cells.[2] In general, these materials are synthesized by two different methods:[3] (i) via precursor routes for insoluble derivatives: nonconjugated or partly conjugated soluble precursor polymers are prepared, purified, and converted as films into the conjugated materials; (ii) via solution polymerization leading directly to a polymer soluble in its conjugated state.

Recently we introduced new PPV derivatives[4] for LED applications that were prepared following the GILCH procedure of polydehydrohalogenation[5] for solution polymerization. These polymers exhibit very good properties (e.g., luminance efficiency, high brightness at low voltage); nevertheless, for these and other polymers of the same type (i.e., soluble PPVs), we noticed strong variations in some of the properties in the PLED application (e.g., luminance efficiency, lifetime in LED application, solubility, gelation temperature) which are not related to the primary structure in an obvious way. Therefore, we became interested in defect structures that are created during the polymerization process.

The mechanism of the GILCH polymerization (cf. Scheme 1) is still under discussion. The first step, which is similar to that of various precursor methods (cf. sulfonium precursor: Wessling route;[6] chloro precursor route;[7] xanthogenate precursor route;[8] sulfinyl precursor route[9]), is the base-induced elimination of HCl which leads to the "real monomer", a quinodimethane derivative[10] (Scheme 1, step 1). For the second step—the polymerization itself (Scheme 1, step 2)—there are two reasonable possibilities: (i) a free radical mechanism, which is claimed for precursor polymerization e.g. by Vanderzande[9] and Wessling,[6] or (ii) an anionic induced polymerization, which is described by Hsieh[7a] for the chloro precursor route. It is even possible that these two pathways compete with each other, depending on the exact reaction conditions. The third (and last) step is the polymer analogous elimination of HCl by a second equivalent of base (Scheme 1, step 3).

Defects in the "regular" polymer chain will especially arise during steps 2 and 3. During step 2 defects such as long-chain branching (i.e., cross-links) and CH_2-CH_2 bond formation in connection with CHCl−CHCl bond formation (which will during step 3′ lead toward single (bisbenzyl moiety) and triple bonds (tolane moiety) or even to chloro−vinyl bonds (Scheme 1, side reaction, step 2′)) are conceivable. Step 3 may lead to substitution instead of elimination (i.e., CH(OR)−CH bond) or to conversion rates below 100%, which results in both single bonds in the main chain and residual chlorine. Some of these possible defects have already been summarized by Schoo and Demandt.[11a] Single- and triple-bond formation was also postulated by Vaeth and Jensen[11b] for unsubstituted PPV. However, no evidence for this defect was found with Raman spectroscopy.

To achieve a better understanding about the occurrence of potential defects, we chose to synthesize a main-chain ^{13}C-labeled PPV: poly[2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-phenylenevinylene], abbreviated OC_1C_{10}−PPV.[4,12] Therefore, we prepared the corresponding monomer in which the CH_2Cl groups were ^{13}C-labeled (cf. Scheme 2).

Experimental Section

Synthesis of Labeled Monomer and Polymers. *Preparation of 1-(3,7-Dimethyloctyloxy)-4-methoxybenzene (**4**).*[4b] In a 2 L four-neck round-bottom flask fitted with dropping funnel, low-temperature condenser, gas outlet, and magnetic stirrer bar, 184.4 g (1.48 mol) of *p*-methoxyphenol (**2**), 275.9 g (1.56 mol, 1.05 equiv) of 1-chloro-3,7-dimethyloctane (**3**), 106.9 g of KOH (85% content purity, 1.62 mol, 1.09 equiv), and 15.04 g (0.1 mol) of sodium iodide were dissolved in 620 mL of dry ethanol and heated to reflux for 64 h with magnetic stirring. The mixture was cooled to room temperature; the reaction solution was decanted from the solid formed and evaporated using a rotary evaporator. The residual solid was taken up in 400 mL of 10% aqueous NaOH solution. It was extracted twice with 400 mL each time of toluene. The organic phases were combined, washed with 100 mL of 10% aqueous NaOH solution, and dried over Na_2SO_4. The solvent was distilled off under reduced pressure with a rotary evaporator. The residue was distilled under reduced pressure (1 mbar, 159−162 °C). A 372.4 g (1.41 mol, 95%) sample of 1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**4**) was obtained as a colorless oil.

Boiling point: 159−162 °C/1 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.82$ (m_c, 4 H; H_{arom}); 3.93 (m_c, 2 H; OCH_2); 3.75 (s, 3 H; OCH_3); 1.79 (m_c, 1 H); 1.59 (m_c, 3 H); 1.30 (m_c, 3 H); 1.15 (m_c, 3 H); 0.93 (d, $J = 6.6$ Hz, 3 H; CH_3); 0.86 (d, $J = 6.7$ Hz, 6 H; $2 \times CH_3$).

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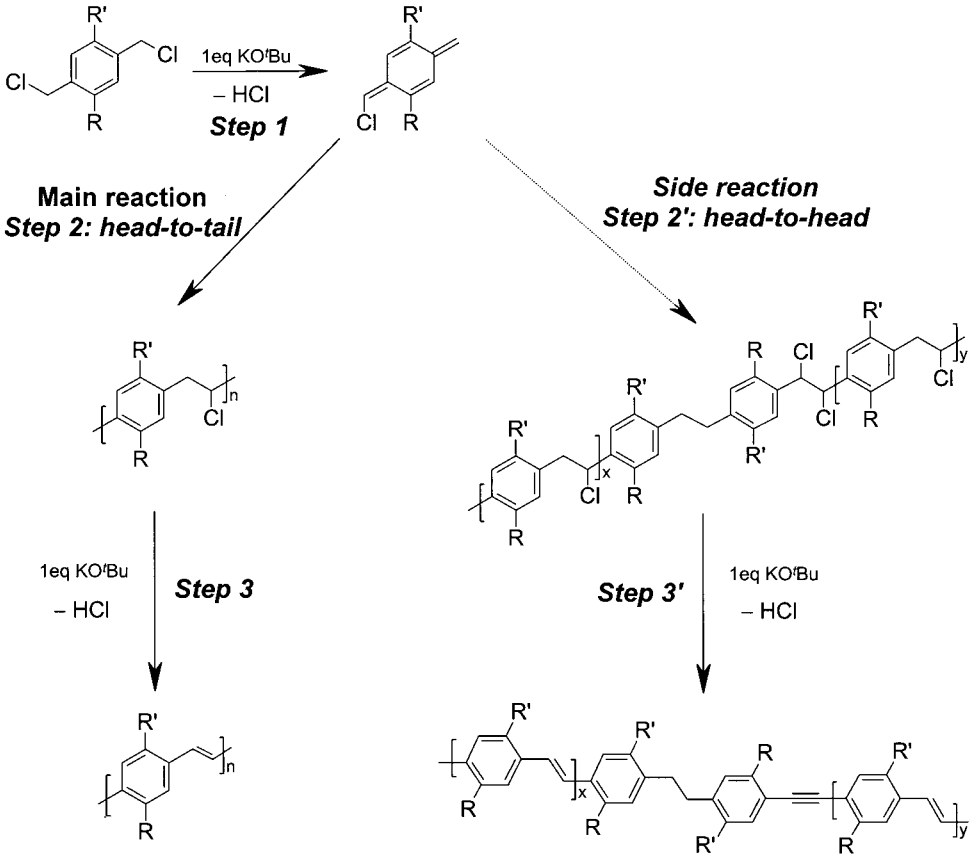
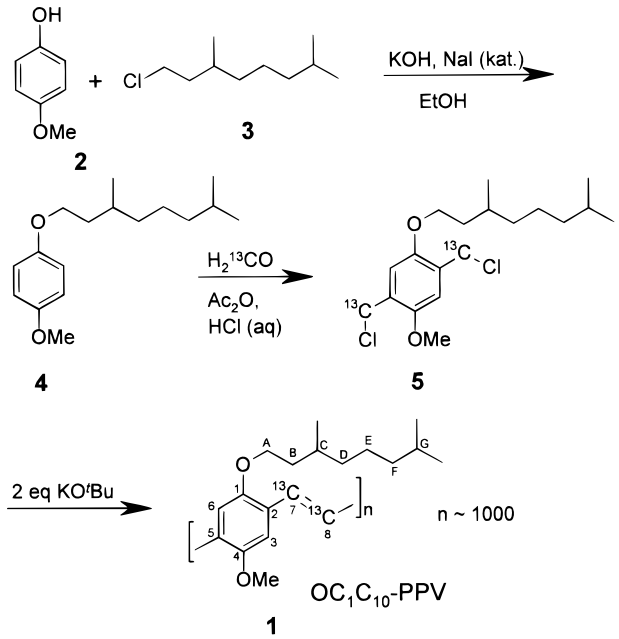
Scheme 1. Reactions and a Potential Side Reaction in the GILCH Polymerization



Scheme 2. Preparation of ^{13}C-Labeled Monomer and Polymer



Warning! Formaldehyde mixtures with HCl form bischloromethyl ether. Take appropriate precautions against this carcinogen.

*Preparation of 2,5-Bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**6**).*[4b] A 304.96 g (1.03 mol) sample of 1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**4**) and 85.38 g (2.84 mol) of paraformaldehyde were placed in a 4 L four-neck flask fitted with mechanical stirrer, reflux condenser, thermometer, and dropping funnel. Under N_2, 490 mL (580.6 g, 5.89 mol) of 37% HCl was added; this gave a yellow suspension. A 990 mL (1070 g, 10.5 mol) aliquot of acetic anhydride was then added dropwise at such a rate that the internal temperature did not exceed 70 °C (time:1.5 h). The last 100 mL was added all at once, which resulted in a temperature rise from 70 to 75 °C; the reaction mixture changed color from beige/brown to reddish. The mixture is stirred for 3.5 h at 70−75 °C. It was then cooled to room temperature while stirring: a light-colored solid crystallized at 32 °C, and the temperature rose to 35 °C. The mixture was allowed to stand overnight at room temperature, resulting in deposition of a light-colored solid. The reaction mixture was admixed with 940 mL of cold-saturated sodium acetate solution (time: about 15 min), and 700 mL of 25% NaOH was then added dropwise at such a rate that the internal temperature did not exceed 30 °C (time: about 35 min). The mixture was then heated to 52 °C (time: about 30 min) and then cooled with an ice bath while stirring rapidly (time: about 30 min). The cream-colored, granular solid was filtered off and washed with 200 mL of H_2O. The solid (451 g) was mixed with 2500 mL of hexane, stirred at room temperature, and then treated with 300 mL of boiling H_2O. The mixture was stirred for 20 min, and the aqueous phase was separated off. The yellowish organic phase was treated with 3 × 300 mL of H_2O; the pH was 5. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was evaporated and crystallized at −20 °C.

The precipitate which resulted (447 g) was filtered off, washed with hexane at −20 °C, and, for recrystallization, dissolved in 1000 mL of hexane at 60 °C. The solution was crystallized at −20 °C, and the solid was filtered off and dried under reduced pressure at room temperature. This gave 279.6 g (0.774 mol, 75%) of 2,5-bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**6**) as a colorless solid.

Melting point: 65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.92$ (m_c, 2 H; H_{arom}); 4.63 (2 s, 4 H; CH_2Cl); 4.02 (m_c, 2 H; OCH_2); 3.85 (s, 3 H; OCH_3); 1.84 (m_c, 1 H); 1.71 (m_c, 1 H); 1.60 (m_c, 1 H); 1.53 (m_c, 1 H); 1.30 (m_c, 3 H); 1.17 (m_c, 3 H); 0.95 (d, J = 6.6 Hz, 3 H; CH_3); 0.87 (d, J = 6.6 Hz, 6 H; 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.1 (s, C-4), 150.7 (s, C-1);

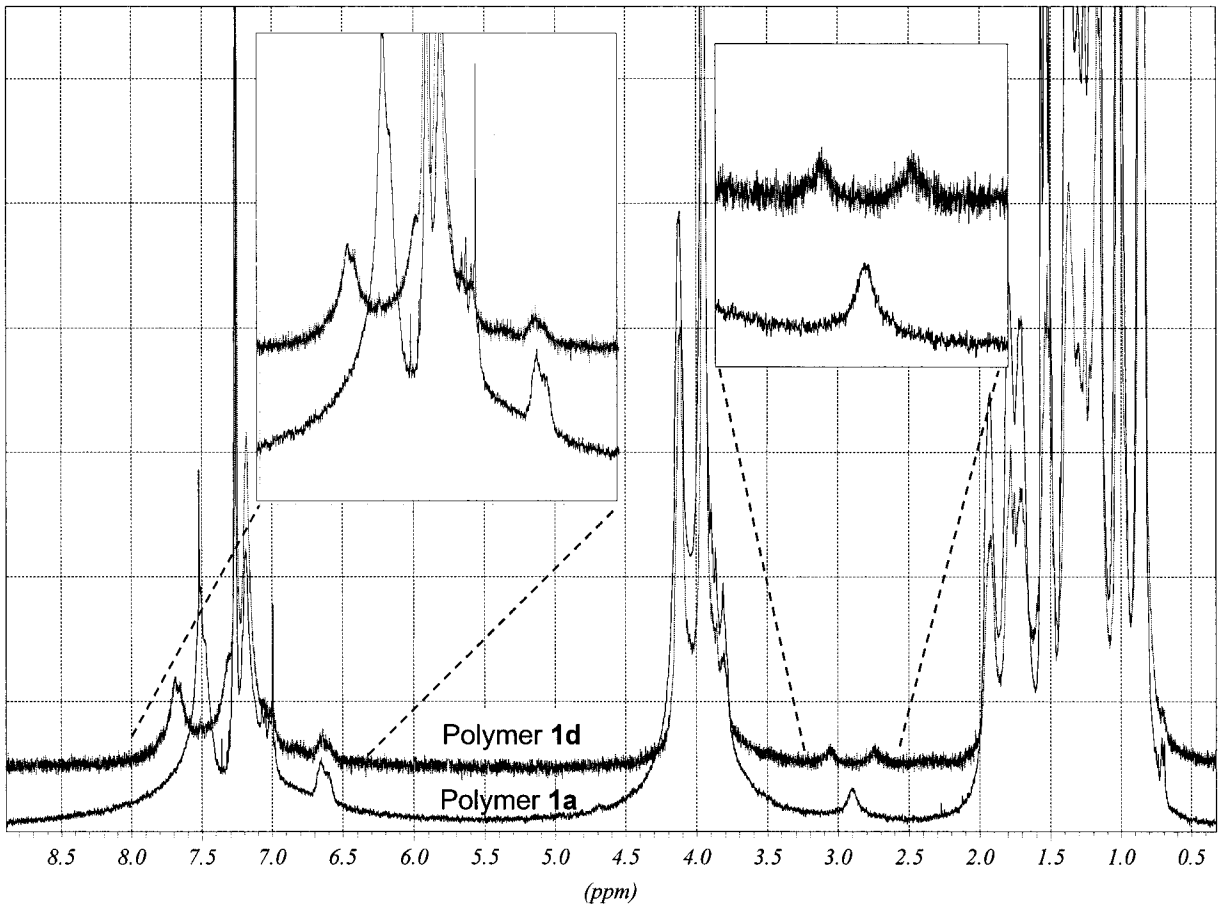


Figure 1. ^{1}H NMR spectrum of polymers **1a** and **1d** (OC_1C_{10}−PPV).

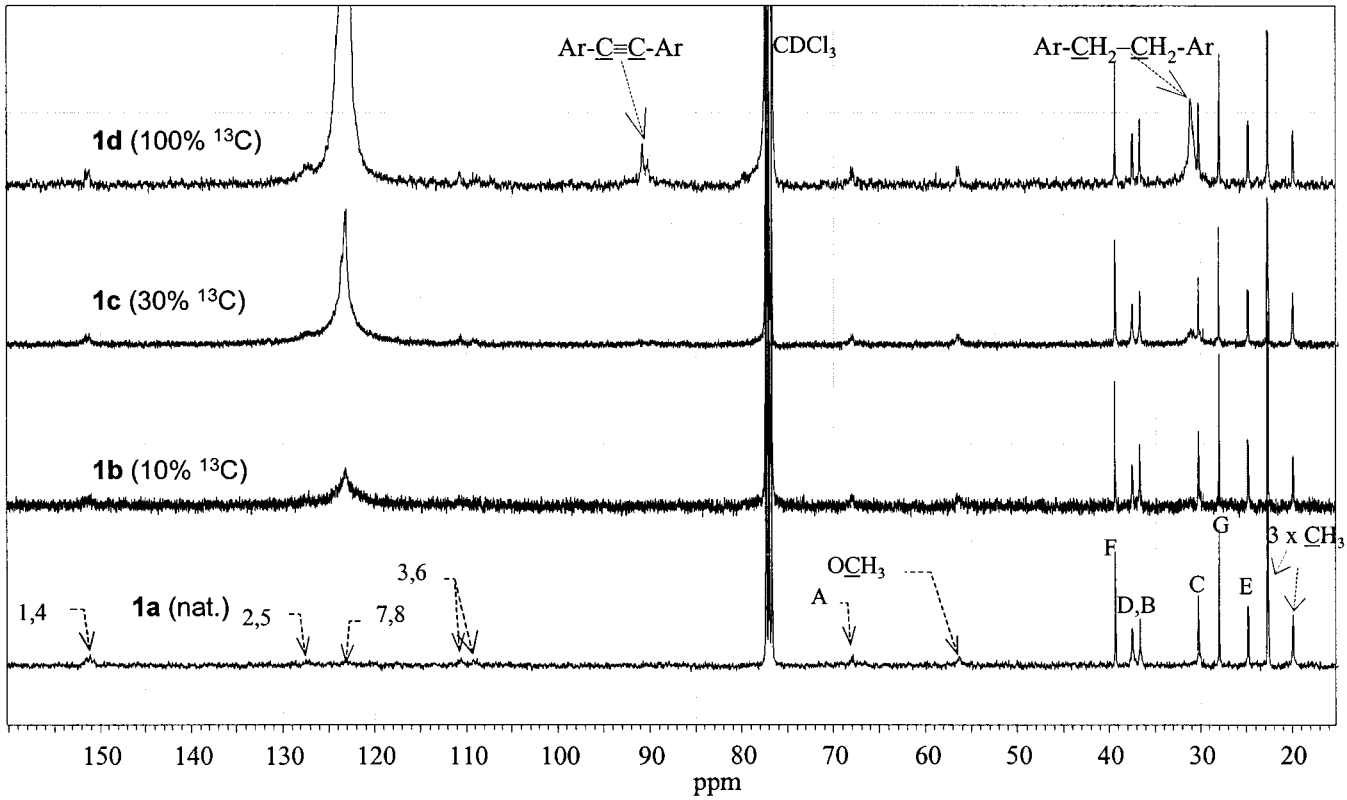


Figure 2. ^{13}C NMR spectra of polymers **1a**−**1d**.

127.1 (s, C-2), 126.8 (s, C-5); 114.4 (d, C-6), 113.3 (d, C-3); 67.5 (t, OCH_2); 56.3 (q, OCH_3); 41.3 (t, 2 × CH_2Cl); 39.2 (t, C-6′); 37.3 (t, C-4′), 36.3 (t, C-2′); 29.9 (d, C-3′); 28.0 (d, C-7′); 24.7 (t, C-5′); 22.7, 22.6, 19.7 (3 × q, 3 × CH_3).

*Preparation of 2,5-Bis(chloro-^{13}C-methyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**5**).* A 632 mg (2.39 mmol) sample of 1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**4**) and 1 mL of 20 wt % ^{13}C-labeled formaldehyde in water (isotopic purity >99%; Deutero, Germany) (6.45 mmol) were placed in a 25 mL three-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and a septum. Under N_2, 1.07 mL (12.9 mmol) of 37% HCl was added and stirred for 3 min. A 4.55 mL (4.90 g, 48 mmol) aliquot of acetic anhydride was then added dropwise over 15 min (the reaction mixture warmed to 60 °C) with a syringe. The temperature was maintained at 70−75 °C for 3 h, and then it was cooled to room temperature while stirring, whereupon a white solid precipitated.

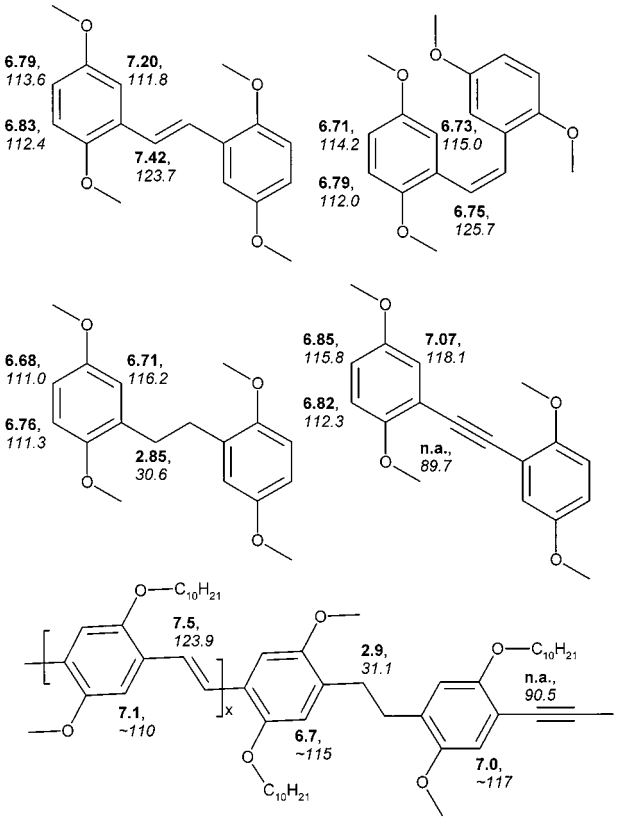
The mixture was then transferred into a separating funnel with 50 mL of ethyl acetate and 20 mL of water; the aqueous phase was extracted twice with 20 mL of ethyl acetate. The combined organic phases were washed twice with 20 mL of water and dried with $MgSO_4$, and the solvent was evaporated with a rotary evaporator. The product was purified by chromatography on silica gel using hexane/ethyl acetate 20:1 and then switching to 10:1. The solid was recrystallized twice from hexane to yield 589 mg (1.62 mmol, 68%) of 2,5-bis(chloro-^{13}C-methyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**5**). By ^{1}H NMR, an isotopic purity of 99.3% was determined. For ^{1}H and ^{13}C NMR, see Supporting Information, Schemes 1 and 2.

*GILCH Polymerization of 2,5-Bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**6**); Preparation of Poly[2-(3,7-dimethyloctyloxy)-5-methoxy-p-phenylenevinylene](=OC$_1$C$_{10}$−PPV **1a**).* A 4 L four-neck flask fitted with mechanical (Teflon) stirrer, reflux condenser, thermometer, and dropping funnel was dried (stream of hot air) and flushed with N_2 . The reactor was then charged with 2.3 l of dry 1,4-dioxane, and the solvent was degassed by passing N_2 through it for about 15 min. The solvent was heated to 98 °C with an oil bath, and 14.0 g (38.7 mmol) of 2,5-bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (**6**) was added as a solid. (The solid was rinsed in with about 10 mL of dry 1,4-dioxane.) A 11.3 g (100 mmol, 2.6 equiv) sample of potassium *tert*-butoxide, dissolved in 100 mL of 1,4-dioxane, was added dropwise to the reaction solution from the dropping funnel over a period of 5 min. During this addition, the reaction mixture changed color from colorless via greenish to yellow/orange, and the viscosity increased significantly. After the addition was complete, the mixture was stirred further for about 5 min at 98 °C; 8.70 g of potassium *tert*-butoxide (77 mmol, 2 equiv) in 77 mL of dry 1,4-dioxane was then added over a period of 1 min, and stirring was continued for 2 h at 96−98 °C. The solution was then cooled to 50 °C over a period of about 2 h. The reaction mixture was finally mixed with 15 mL (260 mmol, 1.5 equiv based on the base) of acetic acid (diluted with the same amount of 1,4-dioxane) and stirred further for 20 min. The solution was then deep orange and the viscosity increased. For the workup, the reaction solution was slowly poured into 2.5 L of intensively stirred water. The resulting mixture was stirred further for 10 min, 200 mL of methanol was added, and the precipitated polymer was filtered off. This was washed with 200 mL of methanol and dried under reduced pressure at room temperature. A 10.04 g (34.8 mmol, 90%) sample of crude polymer was obtained as red fibers.

The polymer was purified by dissolving it in 1.1 L of THF (60 °C), cooling the solution to 40 °C, and precipitating the polymer by dropwise addition of 1.2 L of methanol. After washing with 200 mL of methanol, it was dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol. A 6.03 g (20.9 mmol, 54%) sample of poly[2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-phenylenevinylene] (= OC$_1$C$_{10}$−PPV, **1a**) was obtained as a dark orange, fibrous polymer.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.7−6.5 (br m, 4 H; H_{arom}, olefin-H); 4.5−3.6 (br m, 5 H; OCH_3, OCH_2); 2.1−0.6 (br m, 19 H; aliph H) (see also Figure 1). GPC: THF + 0.25% of oxalic acid; column set SDV500, SDV1000, SDV10000 (from PSS), 35 °C, UV detection at 254 nm, polystyrene standard: M_w = 1.5 × 10^6 g/mol, M_n = 3.1 × 10^5 g/mol. Elemental analysis: calc.: C, 79.12%; H, 9.78%; O, 11.09%. Found: C, 78.88%; H, 9.82%; O, 11.00%; Cl, 25 ppm; K, 41 ppm; Na, 23 ppm.

Scheme 3. Relevant NMR Assignments of Significant Reference Compounds and Defect Structures (H NMR Shifts Are Given in Bold Letters and C NMR Shifts in Italic Letters)



The labeled polymers **1b**−**1d** were prepared analogously by copolymerizing the labeled monomer (**5**) with the unlabeled monomer (**6**) in the molar ratio 10:90 (**1b**), 30:70 (**1c**), and 100:0 (**1d**). The ^{1}H and ^{13}C spectra of these compounds are presented in the Supporting Information or in Figure 2.

Analytical Data. For all compounds ^{1}H and ^{13}C NMR spectra were run on a Bruker AVANCE DPX 400 spectrometer working at a basic frequency of 400 MHz for ^{1}H and of 101 MHz for ^{13}C, respectively. Solutions of ca. 8 mg/mL in $CDCl_3$ (polymers) and ca. 30 mg/mL in $CDCl_3$ (monomeric compounds) were studied at ambient temperature in a 5 mm tube. To obtain a better signal-to-noise ratio, a ^{13}C NMR spectrum of **1d** was run of a 1,1,2,2-tetrachloroethane-d_2 solution at elevated temperature (ca. 363 K) in a 10 mm tube (15 mg/mL). Chemical shifts were referenced to internal tetramethylsilane for protons and to chloroform-d_1 (δ = 77.0) and 1,1,2,2-tetrachloroethane-d_2 (δ = 73.8) for ^{13}C. ^{13}C multiplicities were determined by DEPT135[13a] experiments. For **1a** and **1d** gradient-selected H,C shift correlations (gs-H,C-HMQC[13b] and gs-H,C-HSQC[14]) were carried out. Additionally, a gradient-selected H,C shift correlation experiment optimized for long-range couplings[13c] (gs-H,C-HMBC) was run for **1d**. Parameters for these experiments were chosen to allow close chemical shifts to be distinguished. For the gs-H,C-HMQC and gs-H,C-HSQC the delays for the evolution of $^1J_{C,H}$ were set to 3.45 and 1.72 ms, respectively; for the gs-H,C-HMBC the low pass *J*-filter was 3.45 ms, and an evolution time of 65 ms for $^nJ_{C,H}$ was chosen.

Results and Discussion

Comparing the ^{1}H NMR spectra of polymers **1a** and **1d**, two major differences are obvious (cf. Figure 1): the broad signal centered at 7.5 ppm and the small peak

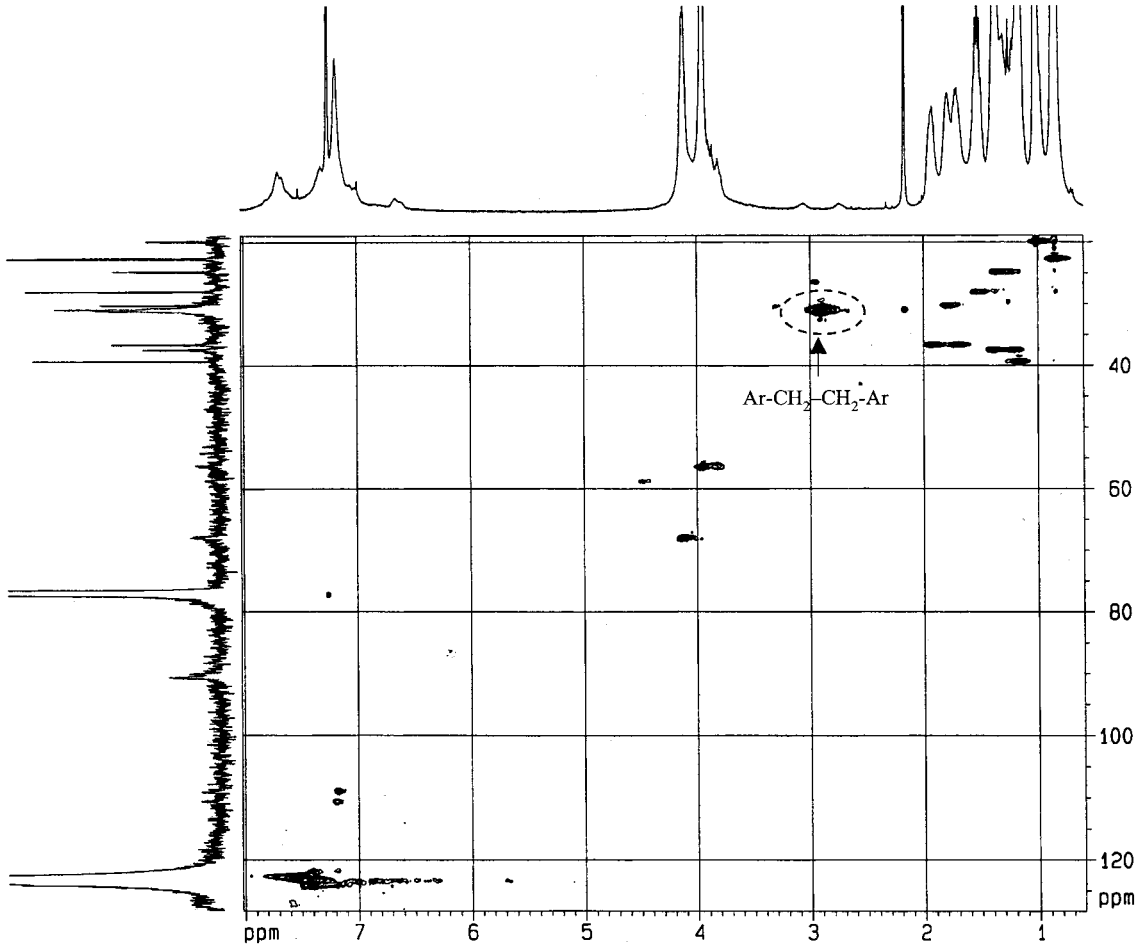


Figure 3. HSQC spectrum of polymer **1d** (100% ^{13}C).

around 2.9 ppm are strongly influenced by labeling. For polymer **1d** the signals split to doublets with an estimated $^1J_{C,H} \sim 130$ Hz (2.9 ppm signal) and ~150 Hz (7.5 ppm signal). This indicates that these two peaks are the chemical successors of the labeled $^{13}CH_2Cl$ groups. For the 7.5 ppm signal the explanation is obvious: it represents the vinylic bond. Its ^1H chemical shifts are in good agreement with a trans double bond as derived from a model compound: 2,2′,5,5′-tetramethoxy-*E*-stilbene (7.42 ppm; cf. Scheme 3 and Supporting Information). For the small peak at 2.9 ppm the situation is more complicated: obviously it reflects an aliphatic, nonconjugated structure within the main chain of the polymer. This ^1H NMR signal is apparent in all polymers prepared following the GILCH procedure,[15] but in varying intensities. However, to the best of our knowledge, this signal has never been mentioned or discussed in the past.[16] Further experiments were done to reveal the nature of this defect (cf. below).

All other peaks show a similar shape in both ^1H NMR spectra (cf. Figure 1). Most of them are well understood: The multiplets around $\delta = 4.0$ and between $\delta = 0.7$ and 2.0 represent the alkoxy side chains. Still unexplained are NMR signals in the vinylic/aromatic region (i.e., the peaks between $\delta = 6.6$ and 7.3). They are definitely not successors of the labeled chloromethyl moieties. Therefore, they have to be assigned to aromatic protons.

For the signal at ~7.1 ppm the interpretation as $H_{aromatic}$ in the regular polymer chain is supported by two arguments: (i) equivalent size to the 7.5 ppm peak (which results from the ratio 2 $H_{vinylic}$ vs 2 $H_{aromatic}$) and (ii) the comparison with the mentioned model compound: 2,2′,5,5′-tetramethoxy-*E*-stilbene (δ(6-H) = 7.20; cf. Scheme 3 and Supporting Information). The smaller signals at ~7.0 and ~6.7 ppm obviously correspond to different structural elements, but (due to the absence of a large $J_{C,H}$ coupling constant for **1d**) they certainly belong to aromatic protons.

The ^{13}C NMR spectra gave a deeper insight in the nature of the polymer structure:

Under standard experimental conditions for the NMR experiment and for natural carbon content, the main chain and also the OCH_3 and OCH_2 carbon atoms are hardly detectable (cf. Figure 2). The remaining side chain atoms, however, exhibit much sharper signals and are therefore more easily detectable. This can be explained by the flexibility of side chains attached to a rigid polymer backbone. All observed signals correspond to the expected structure.

When 10% of ^{13}C is introduced to the polymer (**1b**), a signal that corresponds to a CH=CH bond (123.9 ppm) becomes visible in the ^{13}C NMR spectrum. This chemical shift is in best agreement with that expected for trans double bonds, but it is also similar to that of a cis double bond (see Scheme 3 and Supporting Information for 2,2′,5,5′-tetramethoxy-*E*-stilbene (123.7 ppm) and 2,2′,5,5′-tetramethoxy-*Z*-stilbene (125.7 ppm)). On increasing the level of ^{13}C to 30% (**1c**) and especially to 100% (**1d**), two further broad signals (centered around 90.5 and 31.1 ppm) appear. With the exception of these two peaks, no additional signals were seen. A DEPT135 spectrum

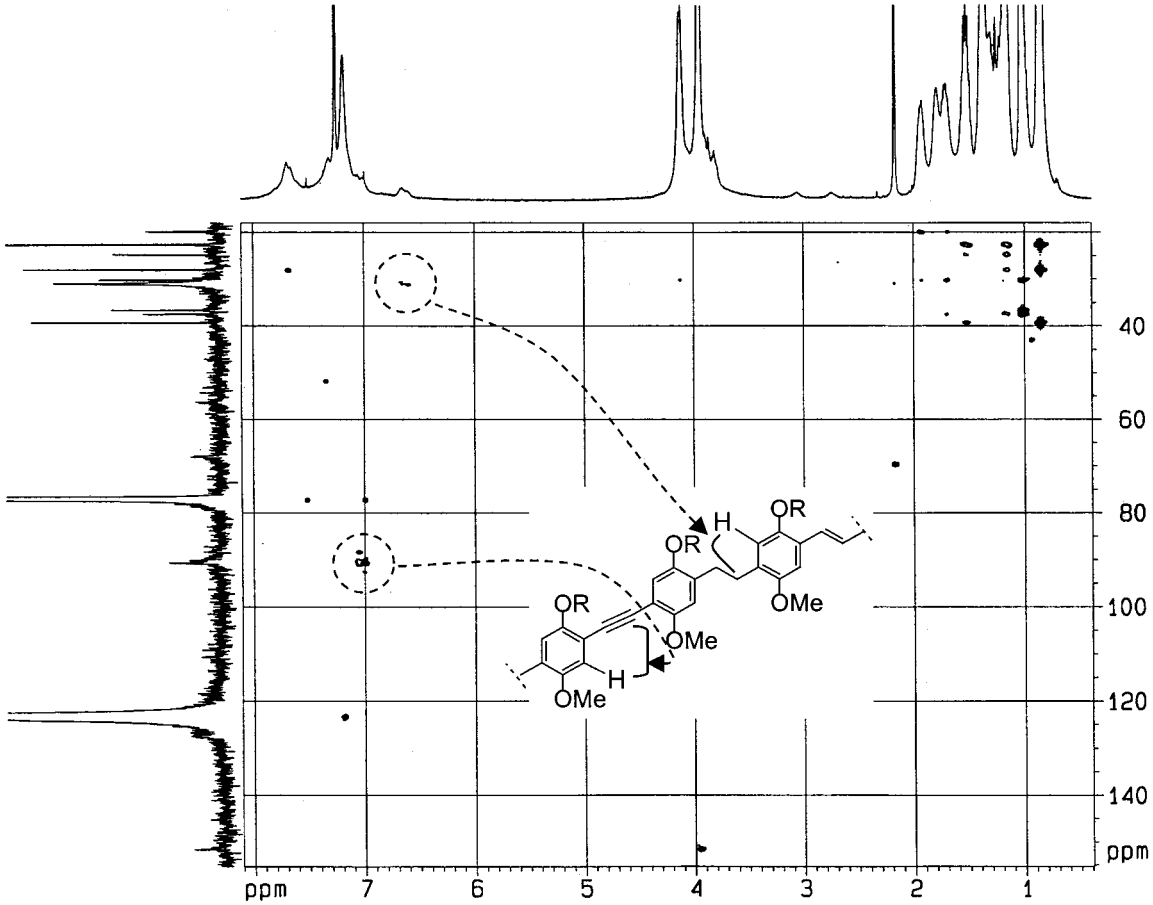


Figure 4. HMBC spectrum of polymer **1d** (100% ^{13}C).

confirmed that the signal at $\delta = 90.5$ originates from a quaternary, whereas that at $\delta = 31.1$ relates to a secondary carbon atom.

An HSQC spectrum (cf. Experimental Section and Figure 3) for **1d** reveals the connection between the ^{1}H NMR 2.9 ppm and the ^{13}C NMR 31.1 ppm peaks (the same is found in HMQC spectrum of polymer **1a**; cf. Supporting Information, Scheme 4). Therefore, these signals have to be assigned to the same structural moiety. From the comparison with a further model compound (2,2′,5,5′-tetramethoxybisbenzyl: ^{1}H, 2.85 ppm; ^{13}C, 30.6 ppm; cf. Scheme 3 and Supporting Information), it is interpreted as a single bond in the main chain, i.e., a bisbenzyl moiety.

The quaternary signal at 90.5 ppm fits to a triple bond in the main chain. This interpretation is supported by (i) a comparison with a model compound (2,2′,5,5′-tetramethoxy tolane (89.7 ppm); cf. Scheme 3 and Supporting Information) and (ii) the proposed reaction mechanism (cf. Scheme 1, side reaction, step 2′): one irregular head-to-head incorporation of one *p*-quinodimethane monomer unit leads (after step 3′ in the reaction sequence) to the formation of an unsubstituted single bond and a triple bond.

Our interpretation for these two ^{13}C NMR resonances is furthermore strongly supported by a gs-HMBC spectrum (optimized for long-range couplings). It enables us to assign the two remaining unidentified signals in the ^{1}H NMR spectrum. The gs-HMBC spectrum (cf. Experimental Section and Figure 4) for polymer **1d** shows that the ^{1}H NMR signals at $\delta = 6.7$ and 7.0 belong to aromatic protons in the neighborhood of the single bond (i.e., cross-peak at $\delta(^{1}H) = 6.7/\delta(^{13}C) = 31.1$) and the triple bond (cross-peak at $\delta(^{1}H) = 7.0/\delta(^{13}C) = 90.5$). These results agree very well with the chemical shifts of our model compounds: for the bisbenzyl [δ(6-H) = 6.71] and for the tolane [δ(6-H) = 7.07] (cf. also Scheme 3 and Supporting Information).

All our investigations show only two defects: a triple and a single bond instead of double bonds which are—via the mechanism (cf. Scheme 1 and related discussion)—logically connected with each other. (From the results of the measurements we are not able to decide whether these two defects are really located on adjacent repeating units or whether they are separated by one or more "normal" double bonds between these moieties.) The occurrence of this defect is consistent with both anionic and free radical polymerization. For this defect we coined the term tolane−bisbenzyl (TBB). From the ^{1}H NMR spectrum the amount of unsubstituted single bonds can roughly be estimated to be 1.5−2.2% (for OC_1C_{10}−PPV). As can be seen from Figure 2 (polymer **1d**), this amount of defect structure can easily be detected using the described method. From the signal-to-noise ratio we estimate that other possible structural elements are at least below 0.5%. No evidence for the presence of a chlorovinyl moiety (precursor for the tolane triple bond) could be found. In addition, the residual organic chlorine in the polymers is below 50 ppm,[17] indicating almost complete elimination of HCl.

Our results show no evidence for the existence of cis double bonds: the model compound (2,2′,5,5′-tetramethoxy-*Z*-stilbene, cf. Scheme 3 and Supporting Information) exhibits the following peaks: ^{1}H NMR: δ(6-H) = 6.73, $\delta(H_{vinylic}) = 6.76$; ^{13}C NMR: $\delta(C_{aromatic}) \sim 112-115$, $\delta(C_{vinylic}) = 125.7$. Therefore, three argu-

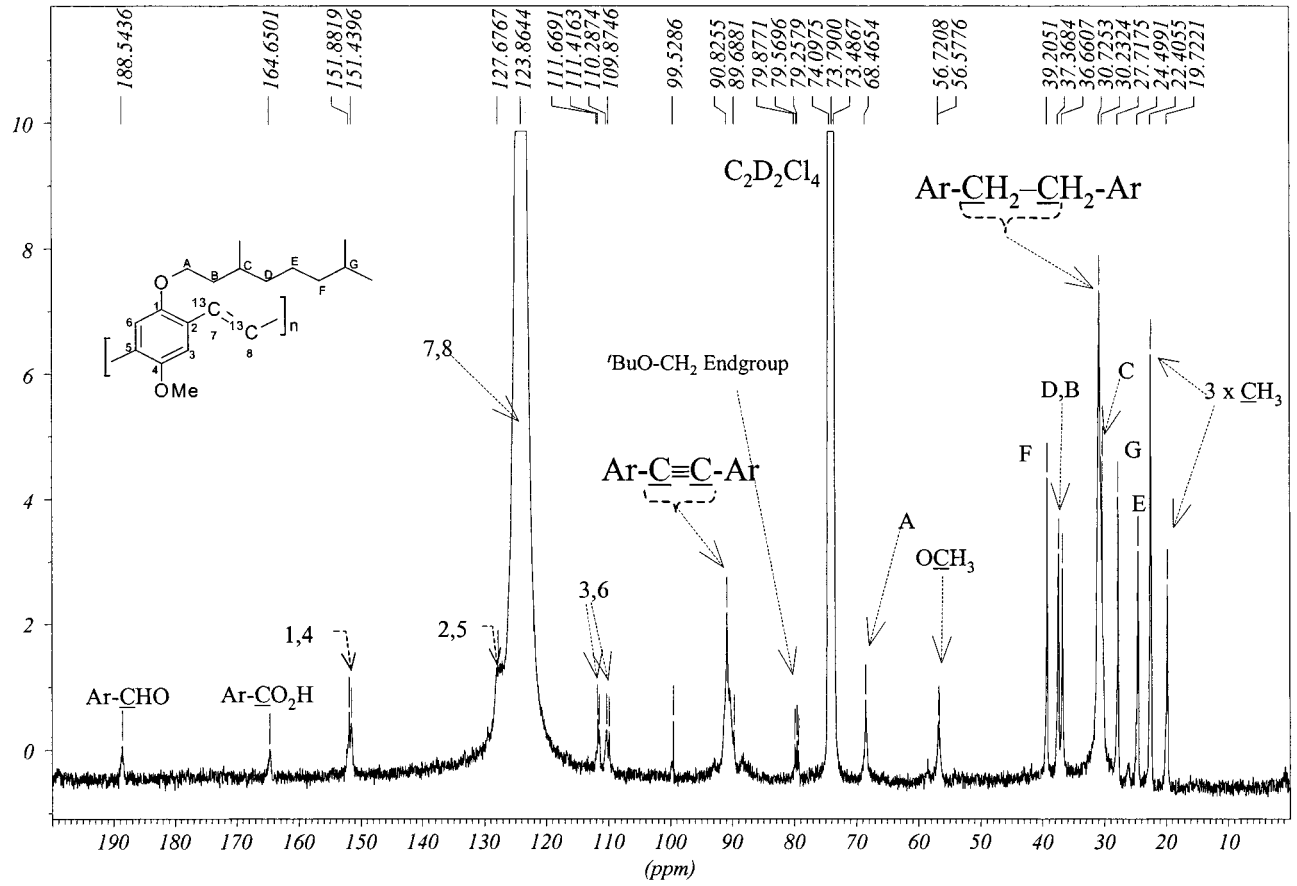


Figure 5. ^{13}C NMR spectrum ($C_2D_2Cl_4$) of polymer **1d** at 90 °C.

ments contradict the presence of larger (i.e., probably more than 1%) amounts of cis double bonds: (i) the absence of a large $^1J_{C,H}$ coupling for the ~6.7 ppm peak (which should—if cis double bonds are existing—represent in part the cis moieties vinylic protons; cf. Figure 1); (ii) the absence of a correlation between this ^1H NMR 6.7 ppm peak with the ^{13}C NMR 123.9 ppm signal (cf. discussion above; this last peak could represent both the trans or cis double-bond vinylic carbon atoms) in the gs-HSQC spectrum of polymer **1d**; (iii) this is even more prominent in the HMQC spectrum of polymer **1a**—the 6.7 ppm peak exhibits a clear correlation to a ~115 ppm ^{13}C NMR signal; this supports also that this 6.7 ppm peak is clearly assigned to $H_{aromatic}$ instead of $H_{vinylic}$ (cf. all the model compounds given in Scheme 3 and in the Supporting Information). The occurrence of a related structural element, i.e., a phenanthrene moiety, was also excluded by comparison of the discussed results with a model compound (1,4,5,8-tetramethoxyphenanthrene; cf. Supporting Information).

With the described experiments only TBB defects were revealed. To get an even clearer insight, a high-temperature experiment with improved signal-to-noise-ratio—due to higher concentration and increased diameter of the tube—was performed (cf. Experimental Section). The results are shown in Figure 5: Four more peaks with low intensity (about a factor of 10 smaller than the TBB peaks, i.e., about 0.2%) are clearly seen. The peaks at 188.5 ppm (Ar−CHO)[18a] and 164.6 ppm (Ar−CO_2H)[18b] are most likely related to degradation of the polymer chain under the influence of oxygen. It is not fully clear whether this oxidation process took place during the reaction, workup, or later during handling or even the NMR measurement. Indications for carbonyl moieties could up to now not be found by infrared spectroscopy of films of PPVs.[19] Formation of those degradation products is therefore more likely to be due to handling of NMR solutions. Tentatively the group of relatively sharp peaks centered around 79.6 ppm is assigned to end groups: Ar−CH_2OR.[18c] Anionic initiation of the polymerization reaction by the base ^{t}BuO$^-$ would result in this structural element.[20] Currently a reasonable explanation for the small peak at 99.5 ppm cannot be offered.

Summary

Using selectively labeled polymers, we have demonstrated the occurrence of only one significant defect structure in GILCH polymerized PPVs: tolane−bisbenzyl moieties (TBB). The amount of this defect is between 1.5 and 2.2% for OC_1C_{10}−PPV.[16] Further structural defects (down to a level of about 0.2%) could not be detected; at this level of sensitivity, we found indications for ether-type end groups and functional groups resulting from deterioration (carbaldehyde and carboxylic acid). We could not find any evidence for cis double bonds and estimate the content to be smaller than 1%. The defects (TBB and ether end groups) are in accordance with the proposed mechanism (cf. Scheme 1), which includes a *p*-quinodimethane and suggests an anionic initiation of the polymerization reaction. The TBB defect would occur in any case, independent of the mechanistic details of the polymerization reaction (free radical or anionic). We think that the TBB defect has a large influence on the performance of the polymers in polymer LEDs. Currently we are working on the consequences of our findings and are optimizing the mi-

crostructure of PPVs to be exploited in LED applications. The results will be published elsewhere.

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Supporting Information Available: NMR data of polymers **1a**−**1d**, NMR data of ^{13}C-labeled monomer **5,** NMR data of model compounds, HMQC spectrum of polymer **1a**, and reaction monitoring data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(16) The intensity of the signal around 2.9 ppm is not influenced by the degree of purification, and therefore the corresponding structure must be an integral part of the polymer. The amount of this defect is dependent on the type of polymer and the polymerization conditions.
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