Toward Controlled Gilch Synthesis of Poly(*p*-phenylenevinylenes): Synthesis and Thermally Induced Polymerization of α-Bromo-*p*-quinodimethanes

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ABSTRACT: It is general consensus that in Gilch polymerizations the 1,4-bis(halomethylene)benzene starting material first changes into an α-halo-*p*-quinodimethane intermediate which then acts as the real active monomer in the subsequent chain growth process. Recently, we could verify the formation of α-chloro-*p*-quinodimethane directly via in-situ NMR spectroscopy at low temperatures. However, quantitative formation of this *p*-quinodimethane was not possible there. Now, we show that even such quantitative conversion into the active monomer is possible if bromomethylene-functionalized starting materials are used instead of their chloromethylene counterparts. Moreover, it is even possible to induce chain growth leading to PPV in a very controlled way by carefully warming the obtained solution of *p*-quinodimethane. In this manner, the temperature can be determined where chain growth starts—and hence thermal energy is sufficient for the initiating process. Finally, we could reconfirm that the chain growth is a radical polymerization here as well, initiated by diradicals formed via spontaneous dimerization of a low number of α-bromo-*p*-quinodimethane monomers. This proof could be provided by quantitatively analyzing the effect of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO): depending on the molar ratio of monomer and scavenger, the chain growth is either retarded or completely prevented.

Introduction

Poly(*p*-phenylenevinylenes) (PPVs) are fascinating semiconductor materials and have an excellent prospect of developing into key compounds in functional devices such as, for example, organic photoconductors and active layers in light-emitting diodes (OLEDs).[1,2] A powerful, versatile, and economically efficient method of PPV preparation is the Gilch route:[3,4] 1,4-bis(halomethylene)benzene derivatives **1** are treated with potassium *tert*-butanolate (KO^{t}Bu), and high-molecular-weight PPVs are formed in these mixtures in yields of typically 70−80%. The negative side of this experimentally very simple process is the characteristic constitutional defects within the PPV chains[5] (which are critical in device applications for efficiency, aging, and fatiguing reasons[6]), their large polydispersity, the tendency to form gels, and the difficulty in controlling molar mass and chain architecture properly. For any systematic optimization of synthetic conditions and materials, on the other hand, it is necessary to understand precisely how the Gilch polymerization operates mechanistically. But unfortunately, there is still controversial discussion about, for example, whether the chains grow via radical and/or anionic mechanisms[3,7] and what the initiating species are. We are therefore analyzing this process in more detail. Recently, we could show that α-chloro-*p*-quinodimethanes **2a** represent the real active monomers.[8] They are formed from starting materials **1a** via dehydrochlorination. Moreover, there is strong evidence that the subsequent chain growth is initiated by diradicals **3a** which form via spontaneous dimerization of a small number of monomer molecules **2a** (Scheme 1).

In contrast to related PPV syntheses such as the Wessling,[9] sulfinyl,[10] or sulfonyl routes,[11] there was no indication of anionic chain growth occurring parallel to the radical one: in our experiments, the reaction proceeds exclusively via radicals—at least for 1,4-bis(chloromethylene)benzene starting materials **1a**, with THF as the solvent, KO^{t}Bu as the base, and temperatures below 80 °C. More recently, and as further support of this mechanistic picture, we could quantify the number of radicals that can be formed in the reaction mixture through detailed analysis of the effect of persistent 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radicals on the progress of this process.[12] Moreover, we could prove—using in-situ NMR spectroscopy at low temperatures—that even at temperatures below −50 °C starting material **1a** changes into α-chloro-*p*-quinodimethane **2a**, but no PPV is formed any more under these conditions.[13] Obviously, thermal energy is still sufficient for dehydrohalogenation at such low temperatures but insufficient for the formation of the initiating radicals **3a**. Only when the mixtures were allowed to warm to room temperature did the change of color, increase in viscosity, and finally gelation indicate formation of PPVs. Keeping in mind these observations, there should be a good chance of decoupling activation of starting material **1**, on the one hand, and polymerization leading to **5**, on the other. And if it is indeed possible to create pure active monomer **2**, modified polymerization processes might enable us to decrease the number of defects within the chains, to tailor molar mass and polydispersity, and to achieve access to novel chain architectures such as block and star systems, for example.

The first challenge to be solved in this respect is identification of reaction conditions where monomer activation is quantitative without simultaneous chain growth. Unfortunately, in all our earlier experiments,[8,12,13] the monomer activation process **1a** → **2a** stopped after approximately 40−70% conversion when temperatures where adhered to where autoinitiation of chain growth is reliably suppressed (<−50 °C). This fact might be due to either insufficient reactivity of **1a** or limited solubility of KO^{t}Bu. Therefore, application of more reactive starting

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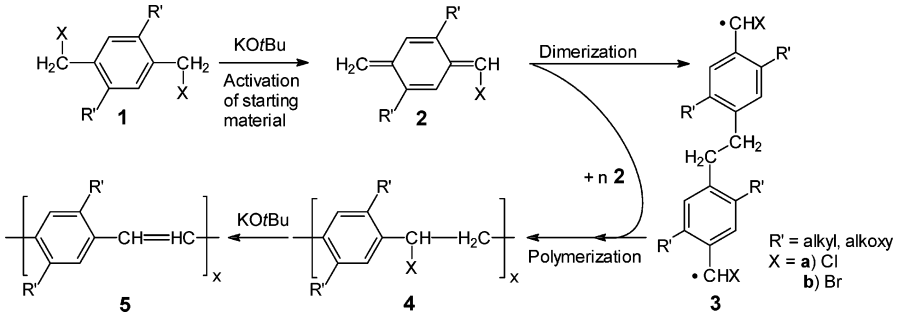
Scheme 1. Current Picture of the Gilch Reaction Mechanism Leading to PPVs 5



materials might be indicated and/or of alcoholates which are more soluble in organic solvents. Alcoholates of improved solubility might be obtained when some methyl groups of the KO^{t}Bu are replaced by larger alkyl moieties. Increased reactivity of **1**, on the other hand, might result when bromomethylene-functionalized starting materials **1b** are used instead of chloromethylene-based species **1a**. When such modifications are undertaken, of course, it must be ensured that the pathway of monomer activation remains unchanged with respect to what we have learned from the chloromethylene-based systems **1a**.

Consequently, in this paper we describe the benefit of using side-chain-substituted 1,4-bis(bromomethylene)benzene derivatives **1b** as starting material. Also, we discuss the consequences when potassium 1-ethyl-1,4-dimethylpentanolate or potassium 1,3-diethyl-1-methylheptanolate is used as the base instead of KO^{t}Bu. Moreover, two types or solubilizing side chains R are compared, i.e., alkyl and alkoxy groups. This was done in order to find out whether there is any effect on monomer activation if oxygen atoms are placed ortho to the reactive functionalities. Because of the limited solubility of *n*-alkyl-/*n*-alkoxy-substituted PPVs, branched 2′-ethylhexyl(oxy) substituents were used. Finally, we study the subsequent chain growth process which sets in when the solutions of the active monomer are allowed to warm and what the consequences are when TEMPO is present in the reaction mixture as a scavenger.

Experimental Section

Materials. All chemicals and solvents were purchased from Acros, Aldrich, and Strem and used without further purification. General procedures were as described recently.[8,12,13] THF-d_8 was purchased from Deutero GmbH, Kastellaun, Germany, and used as received.

Methods. NMR spectra were recorded using a Bruker ARX 300 NMR spectrometer working at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) and on a Bruker DRX 500 NMR spectrometer working at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). δ values are given relative to tetramethylsilane as the internal standard.

1,4-Bis(bromomethylene)-2,5-bis(2′-ethylhexyloxy)benzene (1b^{OR}). *(a) 1,4-Bis(2′-ethylhexyloxy)benzene (**7**).*[14] Under an atmosphere of nitrogen, a mixture of hydroquinone **6** (22.0 g, 0.2 mol), potassium hydroxide (96.0 g, 1.712 mol), and dimethyl sulfoxide (300 mL) is stirred at room temperature for 1 h. 2-Ethylhexyl bromide (152.0 g, 0.788 mol) is added slowly, and stirring at room temperature is continued for a further 4 h. The reaction mixture is poured into ice water (500 mL), the organic layer is separated off, and the aqueous layer is extracted with hexane (4 × 150 mL). The combined organic layers are dried ($MgSO_4$), the solvent is removed, and the oily residue is purified by distillation (bp 165 °C at 0.05 Torr). **7** is obtained as a colorless liquid (61.6 g, 92% yield). ^{1}H NMR ($CDCl_3$): δ = 6.88 (s; 4H, C^{ar}−H), 3.82 (d, 4H, O−CH_2), 1.72 (m, 2H, CH), 1.6−0.93 (m, 28H, other CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ = 153.4 (s; C^{ar}−OR), 115.3 (d; C^{ar}−H), 71.2 (t; O−CH_2), 39.5 (d; CH), 39.4, 30.6, 29.1, 23.9, 23.1 (t; other CH_2), 14.1, 11.1 (q; CH_3).

(b) 1,4-Bis(bromomethylene)-2,5-bis(2′-ethylhexyloxy)benzene (1b^{OR}).[14] A mixture of 1,4-bis(2′-ethylhexyloxy)benzene **7** (30.0 g, 0.089 mol), paraformaldehyde (37.1 g, 1.23 mol), sodium bromide (46.2 g, 0.445 mol), and concentrated acetic acid (250 mL) is stirred and heated to 60 °C. A 1:1 (v/v) mixture of concentrated sulfuric acid and concentrated acetic acid (110 mL) is added slowly, and stirring at 70 °C is continued for a further 4 h. The mixture is cooled to 0 °C; the formed solid is collected, washed with cold water, and recrystallized from hexane. A white powder is obtained (31.1 g, 85% yield); mp 64 °C. ^{1}H NMR ($CDCl_3$): δ = 6.83 (s; 2H, C^{ar}−H), 4.50 (s; 4H, CH_2−Br) 3.86 (d; 4H, O−CH_2), 1.73 (m; 2H, CH), 1.62−0.87 (m; 28H, other CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ = 152.5 (s; C^{ar}−OR), 134.1 (s; C^{ar}−CH_2Br) 120.6 (d; C^{ar}−H), 76.9 (t; O−CH_2), 40.4 (d; CH), 30.0, 29.0, 28.2, 23.5, 23.0 (t; other CH_2), 14.0, 11.2 (q; CH_3).

1,4-Bis(bromomethylene)-2,5-bis(2′-ethylhexyl)benzene (1b^{R}). *(a) 1,4-Bis(2′-ethylhexyl)benzene (**9**).*[15] Under an atmosphere of nitrogen, 2-ethyl-1-bromohexane is added slowly to a mixture of magnesium turnings (41.0 g, 681 mmol), iodine (0.01 g), and diethyl ether (100 mL). Cooling of the reaction flask with ice water might be indicated. After complete addition, stirring and refluxing are continued for a further 1 h. The obtained Grignard solution is slowly added to a mixture of 1,4-dichlorobenzene (100 g, 681 mmol), [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (500 mg, 0.5 mmol), and dry diethyl ether (400 mL). Stirring and refluxing are continued for a further 18 h. Ice water and diluted hydrochloric acid are added until a clear two-phase system is obtained. The organic layer is separated off, and the aqueous one is extracted with *tert*-butyl methyl ether (2 × 300 mL). The combined organic layers are dried ($MgSO_4$), the solvent is removed, and the obtained oil is distilled in vacuum. Colorless oil is obtained (120 g, 65%). ^{1}H NMR ($CDCl_3$): δ = 7.06 (s; 4H, C^{ar}−H), 2.51 (d; 4H, C^{ar}−CH_2), 1.56 (m; 2H, CH), 1.27 (m; 32H, other CH_2), 0.88 (m; 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 138.9 (s; C^{ar}−R), 128.9 (d; C^{ar}−H), 41.1, 39.8, 32.4, 28.9, 25.5, 23.0, 14.1 (t; CH_2), 10.8 (q; CH_3).

*(b) 1,4-Dibromo-2,5-bis(2′-ethylhexyl)benzene (**10**).*[15] At 0 °C, bromine (36.5 mL, 709 mmol) is added to a mixture of **9** (98.2 g, 346 mmol) and iodine (0.01 g). Stirring at room temperature is continued for a further 18 h. The conversion results in compound **10** in a purity sufficient for direct use in the subsequent conversion. ^{1}H NMR ($CDCl_3$): δ = 7.76 (s; 2H, C^{ar}−H), 2.83 (d; 4H, C^{ar}−CH_2), 1.92 (m; 2H, CH), 1.54 (m; 32H, other CH_2), 1.14 (m; 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 140.4 (s; C^{ar}-R), 134.9 (d; C^{ar}−H), 123.3 (s; C^{ar}−Br), 39.3 (d; CH), 39.8, 32.3, 28.7, 25.5, 23.0 (t; CH_2), 14.0, 10.7 (q; CH_3).

*(c) 2,5-Bis(2′-ethylhexyl)terephthaldialdehyde (**11**).*[16] Under an atmosphere of nitrogen, *tert*-butyllithium (1.5 M in pentane, 120 mL, 180 mmol) is added to a cooled (−78 °C) mixture of **10** (82.8 g, 180 mmol). The resulting solution is stirred at the same temperature for 2 h. DMF (12.4 mL, 180 mmol) is added, and the solution is allowed to stir for a further 30 min. Then *tert*-butyllithium (1.5 M in pentane, 360 mL, 540 mmol) and, after another 30 min, DMF (55.5 mL, 540 mmol) are added and stirred again for 30 min. Afterward, the mixture is allowed to warm to room temperature. Subsequently, the mixture is carefully hydrolyzed with water. The organic layer is washed with water; the aqueous

layer is extracted with *tert*-butyl methyl ether (2 × 200 mL). The combined organic layers are dried ($MgSO_4$), and the solvent is removed in vacuum. The obtained **3** (64 g, 99%) is pure enough for direct application in the subsequent conversion. ^{1}H NMR ($CDCl_3$): δ = 10.34 (s; 2H, CHO), 7.67 (s; 2H, C^{ar}−H), 2.94 (d; 4H, C^{ar}-CH_2), 1.52 (m; 2H, CH), 1.23 (m; 32H, other CH_2), 0.83 (m; 12H, CH_3).

*(d) 1,4-Bis(hydroxymethylene)-2,5-bis(2′-ethylhexyl)benzene (**12**).* Under an atmosphere of nitrogen, a mixture of **11** (64.0 g, 178 mmol), lithium aluminum hydride (6.0 g, 162 mmol), and dry THF (250 mL) is stirred at room temperature for 20 h. Upon cooling in an ice bath, the mixture is hydrolyzed by adding sulfuric acid (30%, 30 mL). The resulting mixture is extracted with THF (5 × 100 mL). The combined organic layers are dried ($MgSO_4$) and concentrated down in vacuum. Finally, **12** is purified through filtration over silica gel: a column (5 cm in diameter) is filled with silica gel (10 cm high) suspended in toluene. The solution of the raw product in toluene (200 mL) is allowed to pass through the silica gel. Impurities elute while the desired product remains on the column. Toluene is passed through the silica gel until all byproducts are eluted. Then, the product elutes by changing the eluent to THF. **12** is obtained as a colorless oil (53 g, 82% yield). ^{1}H NMR ($CDCl_3$): δ = 7.15 (s; 2H, C^{ar}−H), 4.52 (d; 4H, CH_2-OH), 2.64 (d; 4H, C^{ar}−CH_2), 2.38 (s; 2H, OH), 1.65 (m; 2H, CH), 1.34 (m; 32H, other CH_2), 0.94 (m; 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 138.5 (s; C^{ar}−R), 136.0 (s; C^{ar}−CH_2OH), 133.0 (d; C^{ar}−H), 40.4 (d; CH), 36.5, 32.6, 31.3, 28.8, 25.9, 23.0 (t; CH_2), 14.0, 10.9 (q; CH_3).

*(e) 1,4-Bis(bromomethylene)-2,5-bis(2′-ethylhexyl)benzene (**1b^R**).* Bis(hydroxymethylene)benzene derivative **12** (40.0 g, 110 mmol) is dissolved in chloroform (100 mL), and HBr (13.4 g, 165 mmol, 98%) is added at room temperature. The resulting mixture is stirred at 50 °C for 3 days and then extracted with chloroform (4 × 50 mL). The combined organic layers are dried ($MgSO_4$) and concentrated under vacuum. The obtained solid is purified via recrystallization from *n*-hexane. Pure **1b^R** is obtained as slightly yellowish crystals (27 g, 50% yield). ^{1}H NMR ($CDCl_3$): δ = 7.11 (s; 2H, C^{ar}−H), 4.48 (s; 4H, CH_2Br), 2.59 (d; 4H, C^{ar}-CH_2), 1.60 (m; 2H, CH), 1.29 (m; 32H, other CH_2), 0.90 (m; 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 138.6 (s; C^{ar}−R), 136.1 (s; C^{ar}−CH_2Br), 133.1 (d; C^{ar}−H), 40.4 (d; CH), 36.5, 32.6, 28.8., 25.9, 23.0 (t; CH_2), 14.1, 10.9 (q; CH_3).

Potassium Alcoholates. *(a) 1-Ethyl-1,4-dimethylpentanol (**16**).* A Grignard solution is prepared by refluxing a mixture of magnesium turnings (12.4 g, 0.51 mol) and 1-bromo-3-methylbutane (75.5 g, 0.5 mol) in dry THF (150 mL) for 4 h. The reaction mixture is cooled to room temperature, and ethyl methyl ketone (36.1 g, 0.5 mol) is added. The solution is refluxed for 12 h and then cooled to room temperature. Water (50 mL) and aqueous HCl (2 N) are added until all inorganic precipitate is dissolved. The aqueous layer is extracted using *tert*-butyl methyl ether (4 × 150 mL). The combined organic layers are dried (Na_2SO_4), the solvent is removed in vacuum, and the remaining raw material is purified by distillation. Alcohol **16** is obtained as a colorless liquid (52.7 g, 73% yield). ^{1}H NMR (DMSO-d_6): δ = 3.78 (s; 1H, OH), 1.50−0.98 (m; CH_2/CH), 0.86−0.76 (m; CH_3). ^{13}C NMR (DMSO-d_6): δ = 70.6 (s; quaternary C), 28.1, 26.2, 22.4, 7.9 (d, q; CH/CH_3), 38.7, 33.6, 32.5 (t; CH_2).

*(b) 1,3-Diethyl-1-methylheptanol (**17**).* A Grignard solution is prepared by refluxing a mixture of magnesium turnings (15 g, 0.62 mol) and 1-bromo-2-ethylhexane (96.56 g, 0.5 mol) in dry THF (150 mL) for 4 h. The reaction mixture is cooled to room temperature, and ethyl methyl ketone (28.84 g, 0.4 mol) is added. The solution is refluxed for 12 h and then cooled to room temperature. Water (50 mL) and aqueous HCl (2 N) are added until all inorganic precipitate is dissolved. The aqueous layer is extracted using *tert*-butyl methyl ether (4 × 150 mL). The combined organic layers are dried (Na_2SO_4), the solvent is removed in vacuum, and the remaining raw material is purified by distillation. The boiling point is 180 °C at 1.3 mbar. Alcohol **17** is obtained as a colorless liquid (44.72 g, 60%). ^{1}H NMR ($CDCl_3$): δ = 1.49−1.11 (m; CH_2/CH), 0.89−0.79 (m; CH_3). ^{13}C NMR ($CDCl_3$): δ = 73.5 (s; quaternary C), 34.7, 26.5; 26.4, 14.1, 10.7, 10.7, 8.2 (d, q; CH/CH_3), 45.3, 45.2, 35.1, 35.1, 34.6, 34.5, 28.9, 28.9, 27.6, 27.9, 23.1 (t; CH_2).

(c) The final conversion of the alcohols **16** and **17** into the potassium alcoholates **18** and **19**, respectively, is carried out by treating them with exactly equimolar amounts of potassium metal under an atmosphere of nitrogen. Stirring for 12 h at room temperature affords bright yellow, highly viscous liquids. Titration using aqueous HCl reconfirms a purity of >99%.

General Procedure for the Preparation of α-Bromo-*p*-quinodimethanes in NMR Tubes; Data Given for 1b^{OR} and KO^{t}Bu as the Starting Materials. 2,5-Bis(2′ethylhexyloxy)-1,4-bis(bromomethylene)benzene, **1b^{OR}** (10.0 mg, 0.03 mmol), is dissolved in THF-d_8 (0.3 mL) and transferred into an NMR tube. KO^{t}Bu (13.5 mg, 0.12 mmol) is dissolved in THF-d_8 (0.7 mL) and put into a 10 mL flask. The NMR tube is cooled to −90 °C, and the solution of KO^{t}Bu is injected slowly under reverse flow of nitrogen into the cooled solution of the starting material **1b^{OR}** using a syringe. Then the tube is cooled with liquid nitrogen. Next, the sample is brought to equilibrium at −80 °C to become liquid again. After shaking gently several times, the reaction mixture was stored in another cooling bath at −90 °C and transferred into the NMR spectrometer with the probe head cooled to −80 °C. As soon as the temperature reaches equilibrium, the active monomer **2b** is formed quantitatively. The same procedure is applied to all the other entries described in this paper.

*NMR Spectra for **2b^{OR}**.* ^{1}H NMR (THF-d_8): δ = 6.57 (H^7), 5.99 (H^5), 5.90 (H^2), 5.51 (H^{8b}), 5.16 (H^{8a}), 3.81 (OCH_2), 1.4−0.82 (other CH, CH_2, CH_3 protons of the side chains). ^{13}C NMR (THF-d_8): δ = 154.3 (C^6), 150.9 (C^3), 137.5 (C^1), 133.9 (C^4), 110.6 (C^8), 103.2 (C^7), 102.1 (C^2), 98.3 (C5), 68.2, 69.5 (t; OCH_2), 30.4 (d; CH), 23.8, 23.7, 15.0, 10.2 (q; CH_3), 35.5, 33.1, 26.4, 24.0 (t; CH_2).

*NMR Spectra for **2b^R**.* ^{1}H NMR (THF-d_8): δ = 6.69 (H^7), 6.59 (H^5), 6.32 (H^2), 5.38 (H^{8b}), 5.30 (H^{8a}), 2.35 (α-CH_2), 1.73−0.88 (m; other CH, CH_2, CH_3 protons of the side chains). ^{13}C NMR (THF-d_8): δ = 141.1 (C^6), 139.0 (C^3), 137.0 (C^1), 134.9 (C^4), 130.7 (C^8), 126.2 (C^7), 114.77 (C^2), 107.2 (C^5), 38.0, 37.6 (α-CH_2), 28.9, 25.7, 19.9, 11.2, 10.5 (CH/CH_3), 33.4, 29.6, 27.7, 24.4, 21.8 (CH_2).

PPV Synthesis at Larger Scale Using Preactivated Monomers 2b. Under an atmosphere of nitrogen, starting material **1b** (200 mg, 10 mmol/L) is dissolved in dry THF. The solution is cooled to −80 °C using an ethanol/liquid N_2 bath. Six equiv of the respective potassium alcoholate, dissolved in dry THF (3.3 mol/L), is added slowly. Stirring at −80 °C is continued for another 30 min. Subsequently, the reaction mixture is allowed to warm to room temperature within 1 h. Stirring at room temperature is continued for a further 4 h. The obtained solution is poured into methanol; the formed solid is collected and dried in vacuum. The yield is almost quantitative.

Results and Discussion

Monomer Synthesis. 1,4-Bis(bromomethylene)benzene derivatives **1b^{OR}** and **1b^R** were the required starting materials for the planned investigations. They have, in addition to their reactive bromomethylene functionalities, two branched side chains which should ensure solubility of the finally resulting semirigid PPVs even with high chain lengths and at low temperatures. It is still a matter of discussion whether oxygen atoms within the side chains influence the process of monomer activation and/or polymer formation. Therefore, we consider alkyl as well as alkoxy side chains in our investigations. The alkoxy-substituted 1,4-bis(bromomethylene)benzene derivative **1b^{OR}** was prepared according to the procedure shown in Scheme 2:[14] hydroquinone **6** was alkylated in DMSO solution using 1-bromo-2-ethylhexane and potassium hydroxide. The resulting hydroquinone dialkyl ether **7** was bromomethylated in a mixture of acetic acid and sulfuric acid using paraformaldehyde and HBr.

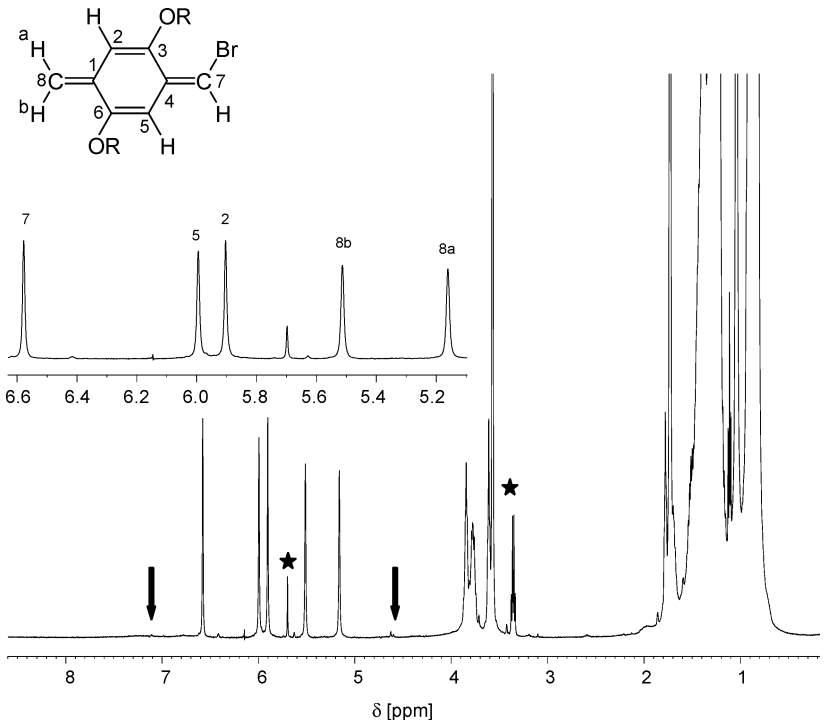
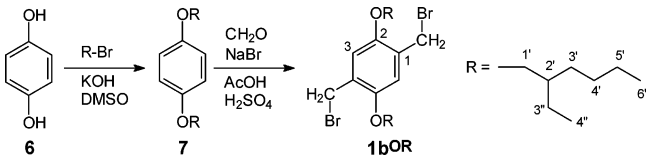


Figure 1. ^{1}H NMR spectrum of a reaction mixture after complete conversion **1b^{OR}** → **2b^{OR}**, obtained at −80 °C using KO^{t}Bu as the base and THF-d_8 as the solvent. Absorptions indicated by arrows correspond to remaining starting material and those by an asterisk to solvent and alcoholate/alcohol.

Scheme 2. Synthesis of Alkoxy-Substituted 1,4-Bis(bromomethylene)benzene Starting Material 1b^{OR}



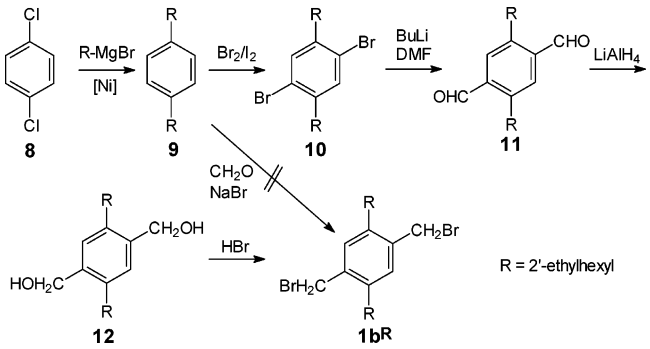
This procedure gave the desired starting material **1b^{OR}** in an overall yield of around 80% and excellent purity (>98%, ^{1}H NMR).

For its alkyl-substituted counterpart **1b^{R}**, on the other hand, the analogous procedure was tested first (Scheme 3). The first step of the reaction sequence, dialkylation of *p*-dichlorobenzene **8,** was easily possible via Kumada coupling using *p*-dichlorobenzene **8**, 2-ethylhexylmagnesium bromide, and a nickel catalyst:[15] dialkylbenzene derivative **9** was obtained in excellent yields and high purity. Its bromomethylation, however, proved to proceed extremely slowly and finally gave very low yields of monofunctionalized product only. Various modifications in the reaction conditions were tested, but so far we have not been able to make this synthesis feasible. Therefore, an alternative procedure was used for the preparation of **1b^{R}** (Scheme 3).

Here, dialkylbenzene derivative **9** was first brominated in its aromatic 1,4-positions. The resulting compound **10** was treated with a mixture of *tert*-butyllithium and dimethylformamide (DMF), leading to dialdehyde **11** in excellent yields. Subsequent treatment of **11** with lithium aluminum hydride in THF solution gave the bis(hydroxymethylene)benzene derivative **12** whose hydroxyl groups were finally exchanged by the required bromine functionalities. This latter step could be carried out by treatment of **12** with HBr in chloroform. After purification, the alkyl-substituted monomer **1b^{R}** was obtained in very high purity (>98%, ^{1}H NMR) in an overall yield of ∼50%.

Potassium Alcoholates of Improved Solubility. Tertiary potassium alcoholates with improved solubility in organic

Scheme 3. Synthesis of Alkyl-Substituted 1,4-Bis(bromomethylene)benzene Starting Material 1b^{R}



solvents were additionally needed for the planned investigations. Improved solubility—and thus lower tendency to crystallize—was expected for alcoholates with long and branched alkyl moieties. Hence, the potassium alcoholates **18** and **19** were selected for the planned investigations. They were obtained according to the synthetic procedure shown in Scheme 4.

In the first step, 3-methyl-1-bromobutane and 2-ethyl-1-bromohexane were converted into the respective Grignard species **14** and **15**. Treatment with methyl ethyl ketone **13** followed by hydrolysis produced the alcohols **16** and **17** in very good yields. NMR characterization confirmed their constitution and high purity. Finally, prior to use, the alcohols were converted into the potassium alcoholates **18** and **19**, respectively, via careful treatment with potassium metal.

Monomer Activation. After having made available all required starting materials and reagents, the next step was a twofold one: first, we had to show that the pathway of monomer activation is the same for the bromomethylene-functionalized starting materials **1b** as was found earlier for the chloromethylene derivatives **1a** (Scheme 1). If this is the case, second, conditions had to be found where the active monomer **2b** is formed in quantitative conversion of **1b** while neither chain

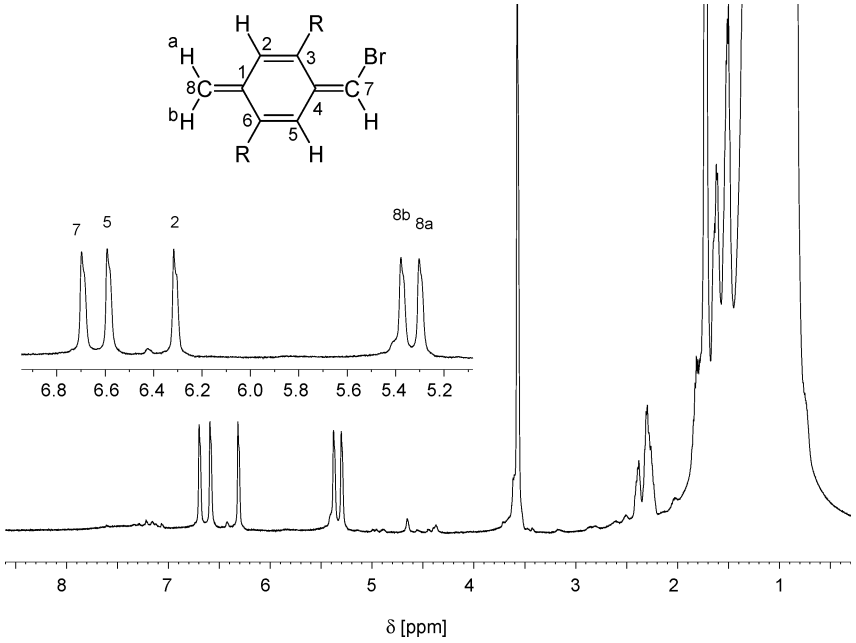
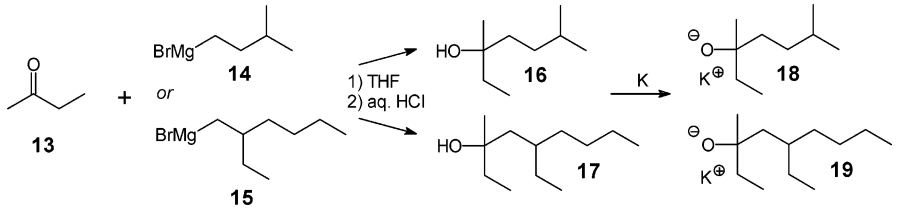


Figure 2. ^{1}H NMR spectrum of a reaction mixture after complete conversion **1b^{R}** → **2b^{R}**, obtained at −80 °C using potassium 1-ethyl-1,4-dimethylpentanolate as the base and THF-d_8 as the solvent.

Scheme 4. Synthesis of Potassium Alcoholates of Improved Solubility in Organic Solvents



growth leading to PPV nor any other side reaction occurs simultaneously.

In order to reconfirm the path of monomer activation for the bromomethylene-functionalized starting materials, a series of experiments were carried out in NMR tubes: compounds **1b$^{OR/R}$** were treated with either of the potassium alcoholates in THF-d_8 solution at different low temperatures. The progress of the conversions was monitored in situ by NMR spectroscopy. Already these trial experiments showed that conversion into the *p*-quinodimethanes **2b$^{OR/R}$** is the dominant reaction here as well. Moreover, it became evident that for the bromomethylene-functionalized starting materials **1b** temperatures of around −60 °C—as were usually applied for the chloromethylene-functionalized systems **1a**—are clearly too high: soon after the first absorptions of **2b**, further broad absorptions additionally appeared in the NMR spectra which could be assigned to PPVs **5**. Therefore, the temperature in the NMR spectrometer was decreased further to completely suppress any PPV formation. Finally, when the conversions were carried out at −80 °C or below, no evidence could be found any more of polymer formation or of any other side reaction, while the activation of starting material **1b** was still ongoing. Moreover, there was not only complete suppression of chain growth at these temperatures but—without having carried out any specific optimization—already more than 90% conversion **1b** → **2b**. This was much more than ever observed for the chloromethylene analogues. On the basis of these results, we concluded that (i) the activation process is the same for starting materials **1a** and **1b**. Moreover, (ii) it could be verified that the activation process is the same for all three potassium alcoholates under investigation here. Last but not least, (iii) we could reconfirm the much higher reactivity of bromomethylene-functionalized starting materials **1b** in the dehydrohalogenation step, but (iv) also the clearly higher tendency of **2b** to polymerize compared to what we know from **2a**.

The next task was to find out the optimum conditions for the conversion of starting materials **1b** into the activated species **2b**. Further NMR experiments were carried out where, at temperatures of slightly below −80 °C, the concentration of starting materials **1b** as well as the concentration and mole equivalents of the three potassium alcoholates were varied systematically. Only minor changes were required with respect to the procedure in the trial experiments to achieve an essentially 100% conversion **1b** → **2b**. Moreover, this conversion was found to be completed within less than half a minute: this was the time required to prepare the NMR measurement. And despite this very fast monomer activation step, no absorptions could be found in the spectra originating from PPVs or other side products even after having stored the solutions of **2b** at −80 °C for more than 1 h. Figure 1 shows a representative ^{1}H NMR spectrum of a reaction mixture obtained after complete conversion of **1b^{OR}** with KO^{t}Bu. All the intense absorptions—except those originating from solvent and alcohol/alcoholate—can be assigned to the protons of **2b^{OR}**. Only very small absorptions, almost invisible in the baseline at $\delta \approx 7.1$ and 4.6 ppm, point toward remaining starting material. This might be due to precipitation of parts of the KO^{t}Bu, causing an imbalance in the available equivalents of starting material and base. The

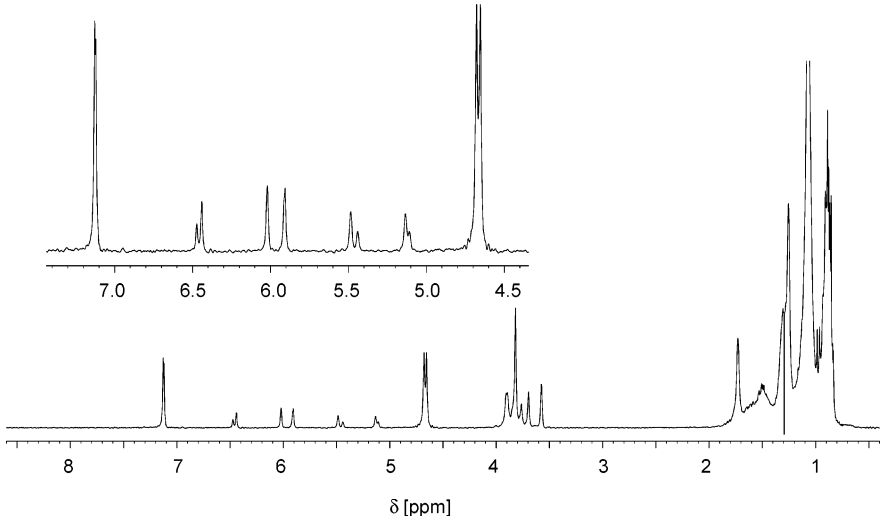


Figure 3. In-situ ^{1}H NMR spectrum of a reaction mixture obtained after almost complete conversion **1a^{OR}** → **2a^{OR}** at a temperature of −60 °C, using KO^{t}Bu as the base and THF-d_8 as the solvent.

same conclusions were drawn from the ^{13}C NMR spectra: there as well, the full signal assignment—based on 2D NMR spectra—clearly supports the formation of **2b^{OR}**.

Complementary to that, Figure 2 shows a ^{1}H NMR spectrum of **2b^{R}** obtained by the treatment of **1b^{R}** with potassium 1-ethyl-1,4-dimethylpentanolate at −80 °C. Here again, almost quantitative conversion into the active monomer **2b^{R}** is evident, and here as well the ^{13}C NMR spectra clearly support this interpretation. However, in contrast to the spectrum shown in Figure 1 where KO^{t}Bu was the base, more "roughness" is clearly visible in the baseline, possibly indicating unidentified side reactions occurring to a minor extent. This might be a consequence of the higher reactivity of **18** and **19** or of their higher solubility—and hence concentration—at those low temperatures. Therefore, application of these new bases might require more specific optimization of the reaction conditions which was, however, not the intention of the present work: this tailored adjustment, and the implications thereof, will be the topic of a subsequent paper.

After having developed appropriate conditions for almost quantitative activation of the bromomethylene-functionalized starting materials **1b$^{OR/R}$**, it was the next question whether this knowledge can be used to achieve a similarly quantitative activation of the chloromethylene-functionalized starting materials **1a$^{OR/R}$**. However, a conversion of more than 60% was achieved in none of these experiments, even after having stored the reaction mixtures at low temperatures for 2 h. Figure 3 shows a representative spectrum recorded after 1 h reaction time at −60 °C of 1,4-bis(chloromethylene)-2-methoxy-5-(2′-ethylhexoxy)benzene, KO^{t}Bu and THF-d_8. The small absorptions correspond to the *p*-quinodimethane formed, while the two intensive signals at $\delta \approx 7.2$ and 4.7 ppm correspond to remaining starting material. When, on the other hand, the temperature was allowed to rise a little in order to accelerate the dehydrohalogenation process, polymerization set in, leading to PPV prior to complete monomer activation.

To summarize, the above findings allow the conclusion that complete conversion of the bromomethylene-functionalized starting materials **1b** into the *p*-quinodimethane species **2b** is possible in THF solution at low temperatures, using all three potassium alcoholates under investigation here. Thus, proper decoupling of monomer activation and chain growth are indeed possible. Moreover, KOtBu seems to be the slightly superior base—at least under standard conditions—compared to the two other alcoholates. Hence, it is predominantly the higher reactivity of the bromomethylene-functionalized starting materials which enables complete conversion into the active monomer. Finally, all studies showed that there is no difference in the rate of monomer activation for starting materials with or without oxygen atoms in the α-position of the solubilizing side chains.

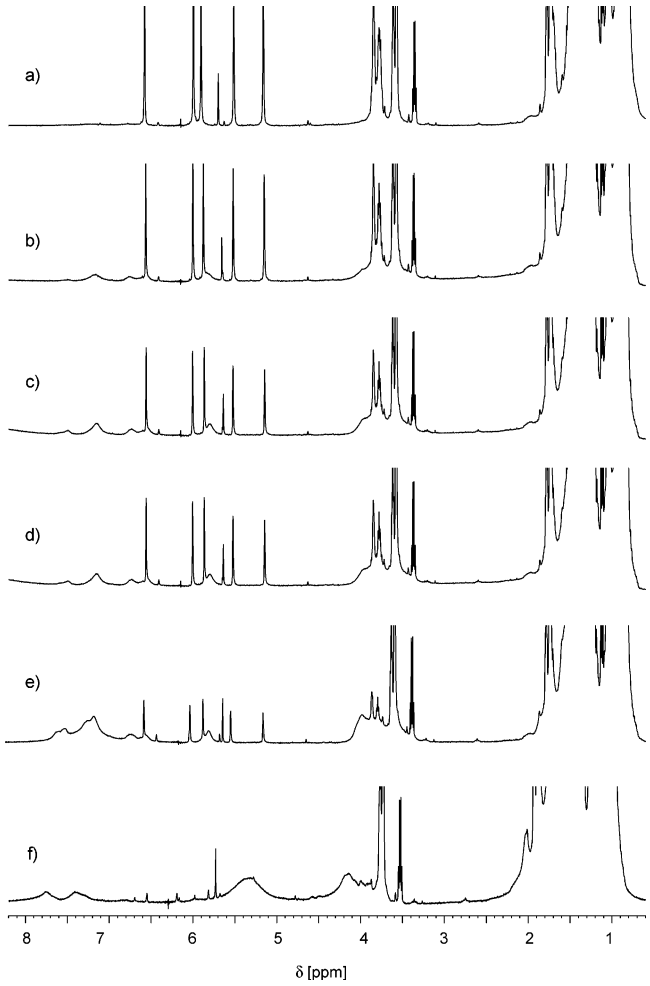
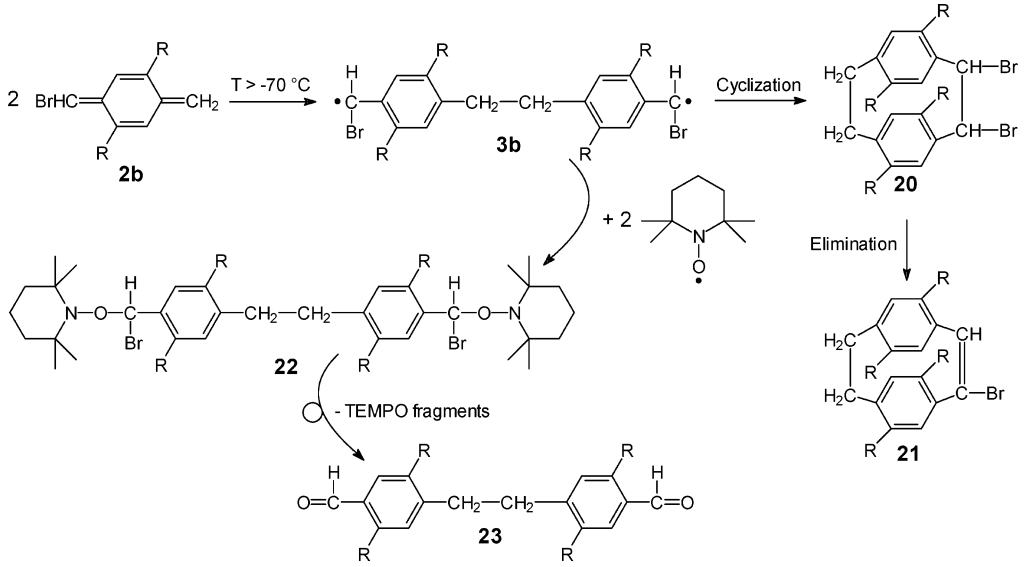


Figure 4. ^{1}H NMR spectra recorded in situ during the warming of a solution of activated monomer **2b^{OR}** (prepared at −80 °C), leading to PPV **5^{OR}**. The temperatures where the spectra were recorded were (a) 193, (b) 203, (c) 213, (d) 223, (e) 233, and (f) 253 K; KO^{t}Bu was the base and THF-d_8 the solvent.

Scheme 5. Cyclization of 3b Gives [2.2]Paracyclophanes 20 and 21, Termination of Dimeric Diradicals 3b by Persistent TEMPO Radicals, and a Possible Consecutive Reaction Leading to Aldehydes



Thermally Induced Polymerization. The next aspect to be analyzed was the question whether it is possible to convert the active (but sleeping at low temperatures) monomers **2b**$^{OR/R}$ into PPV **5** just by allowing the solutions to warm up. When the NMR tubes containing the solution of **2b** were taken out of the NMR spectrometer and slightly warmed, instantaneous change of color to orange, increase in viscosity, and finally gelation indicated rapid formation of PPVs. This interpretation was confirmed by NMR spectroscopy: the spectra showed very broad absorptions at exactly those chemical shifts where high-molecular-weight PPVs should absorb. As these experiments supported the general ability of **2b** to polymerize, the next question was at which temperature chain growth starts. This information could provide deeper insights into the mechanism of the self-initiation process which we believe plays the key role here. Therefore, in subsequent experiments, we allowed the monomer solutions to warm slowly, step by step, within the NMR spectrometer. The warming process could be stopped whenever indicated, and any change in the solution could be monitored directly. Figure 4 shows a series of ^{1}H NMR spectra obtained in such an experiment for a solution of **2b**^{OR}. It can be seen that α-bromo-*p*-quinodimethane **2b**^{OR}, which forms a stable solution at −80 °C, already starts to polymerize at −70 °C! This is evident from the weak and broad but nevertheless clearly detectable absorptions especially in the aromatic region at around $\delta = 6.8-7.8$ ppm. Polymer formation is even faster at −60 °C where broad absorptions are easily detectable in the aromatic region as well as for the O−CH_2 protons at $\delta \approx 4.2$ ppm. Also, there is absorption of increasing intensity at $\delta \approx 5.9$ ppm, which can be assigned to the growing amount of free alcohol formed by the dehydrohalogenation reaction. In parallel with the growth of the polymer absorptions, there is a continuous decrease in intensity of the α-bromo-*p*-quinodimethane absorptions. Later, when the conversion is almost finished, there is a further broadening of all the signals and an apparent loss of signal intensity of the polymer absorptions. This is due to gelation of the reaction mixture which is always observed when Gilch reactions are carried out at low temperatures without stirring. For NMR studies, this has to be accepted but can be easily avoided in lab-scale syntheses.

Finally, when room temperature is reached, the monomer is converted quantitatively, as can be seen by the absence of absorptions of **2b**, and PPV **5** is the predominant product—except for a very small fraction of side products such as [2.2]-paracyclophanes. The origin of the latter is cyclization of dimeric diradicals **3** as was discussed in a recent paper.[8] It should be emphasized that the extent of cyclodimerization is extraordinarily low here: usually, up to 30% of this side product is formed—often unperceived because separated off during precipitation of the polymer.

Encouraged by these very positive results, we transferred the recipe used for the NMR studies to lab-scale experiments: starting materials, concentrations, and temperature program adhered exactly to what was found previously in the NMR studies. The only difference was that vigorous stirring was now possible. And indeed, homogeneous, gel-free solutions of PPVs **5** were obtained using this procedure. Isolation via precipitation in methanol gave fibrous polymers in almost quantitative yields which could be readily redissolved in THF. Hence, representative spectra of the obtained materials were recorded which proved considerable constitutional homogeneity of the PPVs formed in this manner.

To conclude, the above warm-up experiments proved that α-bromo-*p*-quinodimethane **2b** is in fact the real monomer in the Gilch polymerization. Moreover, since oxygen and all other species that might create radicals were carefully eliminated from the reaction mixtures, it is reliable to assume that it is the α-bromo-*p*-quinodimethane **2b** itself which forms the initiator radicals—of course assuming that the reaction is also a radical process. But this had to be shown explicitly here as well.

Effect of Persistent TEMPO Radicals. The above studies provide very strong evidence of radical chain growth, initiated by a small number of radicals which are formed via dimerization **2b** → **3b**. One important argument for the relevance of a radical chain-growth is the formation of [2.2]paracyclophane byproducts such as **20** and **21** (Scheme 5). We interpret their existence as the result of cyclization of the dimeric diradicals **3b**.[8] On the other hand, it was a surprise that first radicals already appear in the reaction mixture—and thus chain growth starts—at −70 °C. Therefore, it was necessary to prove the radical nature of the initiating species in more detail for this system as well. Polymerizations in the presence of TEMPO as a scavenger seem to be the method of choice here:[12] in earlier experiments we had shown that TEMPO causes either temporary inhibition or

complete suppression of polymer formation, depending on its molar ratio with the *p*-quinodimethane. Thus, we carried out further polymerization experiments under the conditions described above, but in the presence of different amounts of TEMPO to deactivate radicals instantaneously after their formation (Scheme 5).

The amount of added TEMPO ranged from 0.5 to 1.5 equiv with respect to starting material **1b**. The experiments reconfirmed, in full agreement with our earlier studies, that precisely 1 equiv of TEMPO is the required amount for permanent suppression of any polymer formation. This result can be rationalized best by Scheme 5: two *p*-quinodimethane molecules **2b** dimerize to give diradical **3b**, and two TEMPO molecules are required to deactivate its two radical centers. If less than 1 equiv of TEMPO is added, on the other hand, the polymerization is initially suppressed for a while, but some polymer is formed later. The quantity of the formed PPV correlates directly with the applied amount of TEMPO. Obviously, it is again dimeric diradical **3b** which is the first species in the systems that behaves like a radical, in full agreement with our mechanistic picture published recently.[12] And indeed, its formation only requires a surprisingly low activation energy.

TEMPO is often used in controlled radical polymerizations for temporary termination of growing polymer chains. Therefore, it was the question whether, in the Gilch reaction as well, TEMPO forms well-defined termini—like those in compound **22**—which can be reactivated at elevated temperatures. Various procedures were therefore tested using in-situ NMR experiments to obtain direct evidence of TEMPO-terminated species like **22**. However, this search has been unsuccessful so far. Instead, strong evidence was found that soon after the termination step **3b** → **22** the TEMPO adducts undergo rearrangements leading to, for example, aldehydes like **22** (Scheme 5): the ^{1}H NMR spectra show intense absorptions at around $\delta \approx 10$ ppm, which is the characteristic region for aldehydes. Also in the ^{13}C NMR spectra, evidence was found of carbonyl carbons at $\delta \approx 185$ ppm. Nevertheless, aldehydes were not the only products when TEMPO was used as a scavenger, but many further secondary products appear of so far unknown constitution. Hence, there is obviously no way for controlled reactivation of the TEMPO-terminated intermediates of a Gilch reaction.

Conclusions

It was the intention of the presented work to find out whether it is possible to decouple monomer activation and polymerization events in a proper way for the Gilch polymerization to PPV. It is shown that—at least so far—this is not possible for chloromethylene-functionalized starting materials while the more reactive bromomethylene counterparts indeed can be converted quantitatively into the α-bromo-*p*-quinodimethanes without any simultaneous start of chain growth. On the other hand, polymerization can be induced very simply just by allowing the cooled (−80 °C) solution of the activated monomer **2b** to warm up slightly to −70 °C. This is not only possible for small entries in the NMR spectrometer but can be transferred directly to the lab scale. Here, constitutionally homogeneous PPV was obtained with a significantly lower amount of [2.2]paracyclophane byproducts. Last but not least, it is shown that the Gilch reaction, as carried out here, is based exclusively on a radical chain growth, and no evidence is found for anionic polymerization. Currently, we are broadening the scope of the findings reported here and analyzing the obtained PPVs with respect to their efficiency, aging, and fatiguing behavior in organic light-emitting diodes.

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