Verification of Radical and Anionic Polymerization Mechanisms in the Sulfinyl and the Gilch Route

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ABSTRACT: Mechanistic studies were performed on the sulfinyl and the Gilch routes, both p-quinodimethane-based polymerizations, toward OC₁C₁₀-PPV. The influence of a combination of additives was investigated to verify the nature of their polymerization mechanisms. In contrast to the sulfinyl route, the Gilch route was irreproducible when performed in THF. Therefore, a reproducible Gilch procedure was developed in dioxane at room temperature. The results of the additives were evaluated by size exclusion chromatography (SEC). All observed effects of both the sulfinyl and Gilch routes are consistent with a radical polymerization mechanism.

Introduction

Over the last 2 decades research in the field of (semi-) conducting polymers has made impressive progress. Thanks to the efforts of synthetic chemists, applied physicists, theoreticians, and materials scientists, plastic electronics such as field-effect transistors (FETs),¹ photovoltaic (solar) cells,² and polymer light-emitting devices (P-LEDs)³ can now (or are almost able to) meet the necessary specifications. The major advantages of polymers are the ease of designing new materials and the low-cost solution processing. Light-emitting displays and integrated circuits, for example, can in principle be manufactured using simple inkjet printer techniques.⁴

At first, the poor processability of conducting polymers hampered their development, as solution processing is in most cases the preferable method for device fabrication. However, several clever synthetic routes (involving precursor and side-chain approaches) were developed to process these polymers in various aqueous and organic solvents, while maintaining their electrical properties. Many of these routes involve p-quinodimethane systems as actual monomers, and can therefore all be described by a general scheme consisting of three steps (Figure 1). The first step is a base-induced 1,6-elimination from a *p*-xylene derivative, **1**, leading to the in situ formation of the *p*-quinodimethane system 2. Second, this intermediate-which can be represented by three structures contributing differently to the character of the molecule-polymerizes spontaneously to the precursor polymer **3**. The conjugated structure **4** is obtained in a third step, directly or after thermal treatment depending on the specific chemical structure of the starting monomer and the polymerization conditions. The synthetic routes differ in the leaving group (L) and a polarizer (P), both functionalities at the benzylic positions. The sulfinyl route uses different L and P functionalities, implying better control over the distinct processes.5

The synthetic route commonly used in industry to obtain poly(*p*-phenylenevinylenes) (PPVs) for use as the

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active layer in P-LEDs and photovoltaic devices is the dehydrohalogenation or Gilch route. Even though this synthesis is currently being applied, the mechanism of the polymerization of these *p*-quinodimethane-based polymerizations is still the subject of an ongoing discord. The two mechanistic possibilities—anionic or radical—have been hard to distinguish. For example, several recent publications on the Gilch route state or favor an anionic polymerization mechanism,^{6,7} while others argue that, e.g., the Wessling route proceeds via a radical mechanism.⁸ Also a previous mechanistic study on the sulfinyl route in *N*-methyl formamide (MMF) led to the conclusion that the main pathway occurs via radicals.⁹

A common way to investigate the nature of a polymerization mechanism is to study the effects of additives. In the current case of in situ monomer formation, additives meant to cause an anionic polymerization reaction (in step 2) could also intervene with the equilibrating carbanion chemistry involved in the pquinodimethane formation (step 1). This definitely complicates a careful interpretation of the observed phenomena. However, clarity on this mechanistic aspect is crucial from an application viewpoint, as control of material properties relies on an understanding of the mechanism.

Previous research on the polymerization mechanism of the sulfinyl route toward PPV precursors concluded that radical as well as anionic polymerization mechanisms can occur simultaneously.¹⁰ Competition between the anionic and radical mechanism strongly depends on the solvent and monomer ring substituents. The anionic mechanism–always yielding oligomers ($M_w < 10\ 000\ g/mol$)—is not observed in protic solvents and is promoted by electron withdrawing substituents. Electron-donating substituents suppress the anionic polymerization in all types of solvent. Mostly, the main polymerization mechanism of the sulfinyl route is radical in nature, and leads to high(er) molecular weight polymer.

The aim of this report is to contribute fundamentally to the ongoing discussion on the polymerization mechanism of *p*-quinodimethane-based routes toward PPV derivatives. The described mechanistic study on poly[2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-phenylenevinylene] (OC₁C₁₀-PPV) aims to make a link between



Figure 1. General scheme for *p*-quinodimethane-based routes toward OC_1C_{10} -PPV.



Figure 2. Representation of the additives used in the mechanistic study.

the polymerization mechanisms of the sulfinyl and the Gilch routes, which are both *p*-quinodimethane-based polymerizations. To elucidate the mechanism of both routes, multiple polymerizations were performed in apolar, aprotic solvents in the presence of different types of additives, and the effects were evaluated by NMR and SEC analyses.

Experimental Section

Materials. The commercially available chemicals Na*t*BuO, tetrahydrothiophene, *n*-butanethiol, MgSO₄, TeO₂, K*t*BuO, TEMPO, carbon tetrabromine, 4-*tert*-butylbenzyl chloride, 4-*tert*-butylbenzyl bromide, 4-methoxyphenol, 2-*tert*-butyl-4-methoxyphenol, 2,6-di-*tert*-butyl-4-methoxyphenol, *tert*-butylbenzyl chloride, *tert*-butylbenzyl bromine, and *p*-methoxyphenol were purchased from Aldrich. The solvents used were all of p.a. quality, purchased from Acros, and used without further purification unless stated otherwise. The solvents THF and 1,4-dioxane were dried over sodium and distilled prior to use. All reactions were performed under a nitrogen atmosphere. 2,5-Bis(chloromethyl)-1-(3,7-dimethyl-octyloxy)-4-methoxybenzene (BCDM) was donated by Covion Organic Semiconductors. All glassware were dried overnight in a drying oven prior to use.

Monomer Synthesis of 1-[2-[(Butylsulfinyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane (and Isomer). A solution of BCDM (70.5 g, 0.195 mol) and tetrahydrothiophene (70 mL, 0.79 mol) in methanol (150 mL) was stirred for 70 h at ambient temperature. The reaction mixture was precipitated in diethyl ether (1700 mL). The

precipitate was collected, washed with n-hexane, and dried under reduced pressure, yielding the corresponding bis(tetrahydrothiophenium) salt as a white hygroscopic solid (96.5 g, 85%). ¹H NMR (D₂O, 400 MHz, numbering based in Figure 5): δ 0.82 (d, J = 3.0 Hz, 6H, H8'), 0.90 (d, J = 6.3 Hz, 3H, H9'), 1.12 (m, 2H, H6'), 1.12 + 1.26 (m, 2H, H4'), 1.28 (m, 2H, H5'), 1.46 (m, 1H, H7'), 1.51 + 1.71 (m, 2H, H2'), 1.51 (m, 1H, H3'), 2.21 (m, 8H, SCH₂CH₂), 3.40 (m, 8H, SCH₂), 3.80 (s, 3H, H13), 4.07 (m, 2H, H1'), 4.41 (s, 4H, ArCH₂S), 7.12 (s, 2H, ArH) ppm. A mixture of NatBuO (7.54 g, 78.4 mmol) and nbutanethiol (7.07 g, 78.4 mmol) in 150 mL of methanol was stirred for 30 min at ambient temperature. This clear solution was added in one portion to a stirred solution of the bis-(tetrahydrothiophenium) salt (46.5 g, 80 mmol) in 250 mL of methanol. After 1 h, the reaction mixture was neutralized with aqueous HCl (1.0 M), and concentrated under reduced pressure. The crude product was diluted with chloroform (250 mL) and filtrated to remove precipitate. The filtrate was concentrated in vacuo, thus yielding a yellow oil. To remove the tetrahydrothiophene, an azeotropic distillation with *n*-octane was repeated three times to obtain 1-[2-[(butylsulfanyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane (and isomer) in a yield of 90%. To obtain the corresponding sulfoxide an aqueous solution (35 wt %) of hydrogen peroxide (19.4 g, 0.2 mol) was added dropwise to a solution of crude thioether (32.8 g, 78.4 mmol) in a mixture of 1,4-dioxane (300 mL), TeO₂ (1.55 g, 9.8 mmol), and some drops of concentrated HCl. After 3 h the reaction was quenched by addition of 250 mL of a saturated NaCl solution. Extraction with chloroform, drying of the combined organic layers over MgSO₄, filtration, and concentration under reduced pressure



remark: the alkoxy side chains are placed at random

Figure 3. Proposed elementary reactions for a radical polymerization mechanism.



Figure 4. Overlay of SEC chromatograms showing suppression of tailing.



Figure 5. Numbering of monomers for NMR data.

afforded a mixture of BCDM (6%), the desired monomer (86%), and the corresponding disulfoxide (8%) as a yellow oil. The reaction mixture was purified by column chromatography (SiO₂, eluent: hexane/ethyl acetate 60/40) to give pure monomer as a light yellow oil (82%), which solidified upon standing. ¹H NMR (CDCl₃, 300 MHz, numbered according to Figure 5): δ 0.83 (d, J = 6.6 Hz, 6H, H8'), 0.90 (d, J = 6.3 Hz, 3H, H9'), 0.89 (t, J = 7.2 Hz, 3H, H12), 1.12 (m, 2H, H6'), 1.12 + 1.26 (m, 2H, H4'), 1.28 (m, 2H, H5'), 1.41 (m, 2H, H11), 1.46 (m, 1H, H7'), 1.51 + 1.71 (m, 2H, H2'), 1.51 (m, 1H, H3'), 1.71 (m, 2H, H10), 2.58 (m, 2H, H9), 3.65 (s, 3H, H13), 3.95 (m, 2H, H1'), 3.79 + 3.78 (dd, $J_{AB} = 9.6$ Hz, 2H, H8), 4.63 + 4.55 (dd, 2H, H7), 6.80 (d, J = 2.1 Hz, 1H, H6), 6.89 (d, J = 3.9 Hz, 1H, H3) ppm. IR (KBr): 2959, 2916, 2846(CH₃, CH₂ asymm), 1443 (C-H), 1070 (*S*(*O*)), 847 (1,4-subst. arom.) cm⁻¹. MS (EI, m/z, relative intensity (%)): 431 ([M + 1]⁺, 100), 395 ([$C_{23}H_{39}O_{3}S$]⁺, 10), 325 ([$C_{19}H_{30}CIO_2$]⁺, 30), 163 ([$C_{10}H_{11}O_2$]⁺, 30).

General Sulfinyl Polymerization Procedure in THF at Ambient Temperature: Preparation of Poly-[2-(3,7-dimethyloctyloxy)-5-methoxy-p-phenylenevinylene] (OC1C10-PPV). Prior to reaction a 100 mL threeneck flask with Teflon stirrer and reflux condenser was flushed with nitrogen gas for about 30 min. The solvent (20 mL) was degassed by bubbling N₂ through it for another 15 min. Another 5 mL of dry THF was used to rinse in 0.5 mmol (0.2153 g) of the monomer providing a monomer concentration of 0.02 M. In the case of polymerizations in the presence of an additive, at this stage the additive was added to the monomer solution in the amount of 0.5 equiv, based on the amount of monomer (e.g., 0.25 mmol TEMPO: 0.040 g). Polymerization was initiated by addition of 1.3 equiv (0.65 mmol, 0.073 g) of solid potassium tert-butoxide. After 2 h at ambient temperature, pouring the mixture into 250 mL of ice-water stops the reaction. Excess base was neutralized by addition of 1.0 M aqueous hydrochloric acid, followed by extraction with chloroform. The combined organic layers were concentrated under reduced pressure, and the precursor polymer was redissolved in 25 mL of toluene. Thermal elimination to the conjugated polymer took place during 3 h of reflux. At about 40 °C a dropwise addition of 30 mL of methanol caused the polymer

 Table 1. Results of Standard and Additive Experiments on the Sulfinyl Route in THF^a

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	yield (%)	$M_{\rm w}$ (g/mol)	$M_{\rm n}$ (g/mol)	PD
standard ^b	35	178 000	47 300	3.7
	55	226 000	46 500	4.9
<i>t</i> BuPhCH ₂ Cl	53	213 000	52 100	4.1
	55	205 000	50 300	4.0
<i>t</i> BuPhCH₂Br	34	141 000	47 300	3.0
	51	130 000	39 600	3.3
TEMPO	0			
	0			
CBr ₄	6	25 300	10 500	2.4
	7	38 500	19 400	2.0
<i>t</i> BuMeOPhOH	7	11 900	4 900	2.4
	6	12 400	4 600	2.7

^{*a*} Polymerization conditions: solvent = dry THF; ambient temperature; 2 h; amount of additive, 0.5 equiv; KtBuO added as a solid. ^{*b*} Standard: general polymerization procedure in which no additives are used.

to precipitate (except in the case of *tert*-butylmethoxyphenol addition, where precipitation by addition of methanol only occurred after evaporation of toluene). The precipitated polymer was recovered by filtration, washed with methanol and dried under reduced pressure at room temperature. Residual fractions were concentrated from the filtrate in vacuo. ¹H NMR (CDCl₃, 300 MHz): δ 0.6–2.0 (br, 19H, H2'-H9'), 3.7–4.0 (br, 3H, H13), 4.0–4.2 (br, 2H, H1'), 7.1–7.3 (br, 2H, PhC*H*= *CHP*h), 7.3–7.6 (br, 2H, H3 + H6) ppm. IR (KBr): ν 2957, 2925, 2860, 1510, 1469, 1395, 1217, 1028, 872 cm⁻¹. Corresponding yields and polymer characteristics like $M_{\rm n}$, $M_{\rm w}$, and polydispersity values are listed in Table 1.

General Gilch Polymerization Procedure in THF at Ambient Temperature toward OC₁C₁₀—PPV. The general procedure for sulfinyl polymerization in THF was followed except for the addition of the base and the elimination procedure. In the case of polymerizations in the presence of an additive, the additive was added to the monomer solution in an amount of 0.5 equiv (e.g., 0.25 mmol *t*BuPhCH₂Br: 0.060 g). Polymerization of 0.18 g (0.5 mmol) of solid 2,5-bis-(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene was initiated by addition of 1.3 equiv (0.65 mmol; 0.073 g) of solid potassium tert-butoxide via an elbow. In most cases the viscosity increased significantly while the reaction mixture turned from colorless to yellow/orange. After 10 min, 3.3 equiv (1.65 mmol; 0.185 g) of solid potassium tert-butoxide was added to start elimination, and the reaction mixture became a deep orange-except for the TEMPO experiments where a yellow color with an orange tone was preserved. Stirring was continued for 2 h. For workup the solution was poured in icewater under vigorous stirring. Aqueous hydrochloric acid (3.5 mL of 1.0 M) and methanol (2.5 mL) were added, and the precipitated polymer was recovered by filtration over a glass filter. The red fibrous polymer was washed with methanol and dried under reduced pressure at room temperature. Residual fractions were concentrated in vacuo. ¹H NMR of the polymer was identical to the one described previously.

General Purification Procedure in THF. The polymers were purified using a similar procedure to that described in ref 11. The polymer was dissolved in 25 mL of THF and heated to 68 °C for 2 h. The solution was cooled to 40 °C and a dropwise addition of methanol caused the solution to become red due to precipitation of the polymer. The precipitated polymer was recovered by filtration, washed with methanol and dried under reduced pressure at room temperature. Corresponding polymer yields and M_n , M_w , and polydispersity values after purification are listed in Table 2.

Gilch Polymerizations in 1,4-dioxane toward OC₁ C_{10} – **PPV at Elevated Temperature.** This procedure is based on the general procedure for Gilch polymerization (as reported previously for Gilch in THF). This time dry 1,4-dioxane was used as the polymerization solvent, and reactions were executed at a temperature of 98 °C using an oil bath. A variation of base amounts was tested: changing the first K*t*BuO portion

 Table 2. Experimental Results on the Gilch Route in THF: After One Purification^a

	yield (%)	$M_{ m w}$ (g/mol)	$M_{\rm n}$ (g/mol)	PD
standard ^b	38	695 000	66 800	10
	23	1 100 000	71 400	15
	44	530 000	55 100	10
	56	772 000	58 800	13
	43	928 000	52 000	18
<i>t</i> Bu¢CH₂Cl	39	534 000	34 300	16
<i>t</i> Bu¢CH₂Br	42	1 280 000	72 300	18
	50	781 000	57 400	14
TEMPO	0			
	0			
CBr_4	50	336 000	29 300	11
	32	266 000	43 300	6
	56	427 000	56 000	8

^{*a*} Polymerization conditions: solvent = dry THF, ambient temperature, 2 h, amount of additive: 0.5 equiv, KtBuO added as a solid; purification in THF for 2 h at 68 °C. ^{*b*} Standard: general polymerization procedure in which no additives are used.

 Table 3. Results of Gilch Polymerizations in Dioxane at

 98 °C Using Various Relative Base Amounts^a

K <i>t</i> BuO portion 1 (equiv)	K <i>t</i> BuO portion 2 (equiv)	yield (%) ^b	M _w (g/mol)	Mn (g/mol)	PD
1.3	3.3	47 (54)	805 000	77 100	10
		33 (36)	748 000	92 000	8
2.6	2.0	24 (44)	903 000	80 200	11
		32 (39)	707 000	76 000	9

^{*a*} Polymerization conditions: solvent = dry dioxane; 98 °C; 2 h; no additive; KtBuO added as a solid; purification in THF for 2 h at 68 °C. ^{*b*} Number in parentheses: yield before purification.

from 1.3 to 2.6 equiv (initiation) and the second KtBuO portion from 3.3 to 2.0 equiv (elimination). The polymers were subjected to a general purification procedure in THF.

General Gilch Polymerization Procedure in 1,4-dioxane toward OC1C10-PPV at Ambient Temperature. This procedure is based on the general procedure for Gilch polymerization in THF, only the solvent THF was replaced by dry 1,4-dioxane. In the case of polymerizations in the presence of an additive, the additive was added to the monomer solution in an amount of 0.5 equiv (e.g., 0.25 mmol *t*BuPhCH₂Cl: 0.046 g). Polymerization was initiated by addition of 1.3 equiv (0.65 mmol; 0.073 g) of solid potassium *tert*-butoxide via an elbow. After 10 min, 3.3 equiv (1.65 mmol; 0.185 g) of solid potassium tert-butoxide was added and the viscosity increased significantly while the reaction mixture became a deep orange. Within the hour a phase separation between a red polymer lump and a yellowish solution was completed. Nevertheless, stirring was continued for 2 h, and then the polymerization temperature was raised to 98 °C (2-12 h) until a homogeneous solution was obtained. For workup the solution was cooled to 40 °C, and during vigorous stirring 25 mL of water was added slowly. Also 3.5 mL of 1.0 M aqueous hydrochloric acid and 2.5 mL of methanol were added, and the precipitated polymer was recovered by filtration. It was washed with methanol and dried under reduced pressure at room temperature. Next, the polymer was subjected to a standard purification procedure in THF. Information on SEC results and polymer yields are listed in Table 6. Residual fractions were dried under reduced pressure. In the case of the additional experiment with TEMPO an additional amount of 0.2 equiv (0.016 g) of TEMPO was added to the reaction mixture together with the second portion of base (3.3 equiv added as a solid).

Additional Experiments on Additives 9, 10, and 11. A 100 mL three-neck flask with Teflon stirrer, reflux condenser, and septum was flushed with N₂. Two base solutions were prepared under a nitrogen atmosphere: the first of 1.3 equiv (0.65 mmol; 0.073 g) of K*t*BuO in 4 mL of dioxane, and a second containing 3.3 equiv (1.65 mmol; 0.185 g) of K*t*BuO in 7 mL of dioxane. Additives **9, 10,** and **11** were added to the first base

 Table 4. Results of Gilch Polymerizations in Dioxane at

 Ambient Temperature^a-at Various Purification Levels

entry	purification level	yield (%)	$M_{\rm w}$ (g/mol)	$M_{\rm n}$ (g/mol)	PD
1		94	3 160 000	77 000	41
2	THF, 68 °C	89	2 020 000	64 300	32
3	dioxane, 98 °C	74	754 000	94 000	8
4	dioxane, 98 °C	78	816 000	130 000	6
5	THF, 68 °C	74	813 000	111 000	7

^{*a*} Polymerization conditions: solvent = dry dioxane; ambient temperature; 2 h; no additive; KtBuO added as a solid.

Table 5. Effect of Purification in THF on SECCharacteristics of Gilch Polymers Synthesized in
Dioxane^a

PD	$M_{\rm n}$ (g/mol)	$M_{\rm w}$ (g/mol)	additive	entry
17	46 000	788 000	none	1
8	94 000	754 000		2
19	32 000	606 000	<i>t</i> BuPhCH ₂ Cl	3
10	60 000	582 000		4
6	9 600	59 000	CBr_4	5
4	19 000	73 000		6
1 1	94 000 32 000 60 000 9 600 19 000	754 000 606 000 582 000 59 000 73 000	<i>t</i> BuPhCH ₂ Cl CBr ₄	2 3 4 5 6

^{*a*} Odd entries: values after purification in dioxane and before purification in THF at 68 °C. Even entries: values after the purification in THF at 68 °C. Polymerization conditions: solvent = dry dioxane; ambient temperature; 2 h; amount of additive,0.5 equiv; KtBuO added as a solid. Purification: first for 2–12 h in dioxane at 98 °C; second in THF at 68 °C for 2 h.

Table 6. Results of Standard and Additive Experimentson the Gilch Route in Dioxane at Ambient Temperature:After Thermal Treatment^b

	yield (%)	$M_{\rm w}$ (g/mol)	$M_{\rm n}$ (g/mol)	PD
standard ^c	78 (85)	754 000	94 000	8
	74 (78)	797 000	109 000	7
	85 (86)	650 000	93 200	7
<i>t</i> BuPhCH ₂ Cl	76 (77)	582 000	60 100	10
	80 (83)	720 000	73 000	10
<i>t</i> BuPhCH ₂ Br	80 (83)	655 000	98 000	7
	80 (83)	533 000	90 000	6
CBr ₄	75 (100)	73 300	19 300	4
	83 (100)	85 000	26 000	3
TEMPO	21 (33)	179 000	40 000	5
	26 (38)	227 000	53 000	4
MeOPhOH	12 (30)	1 510 000	87 100	17
	3 (22)	16 000	6 200	3
	10 (39)	679 000	48 000	14
<i>t</i> BuMeOPhOH	8 (14)	479 000	49 000	10
	2 (20)	58 100	15 300	4
	3 (40)	190 000	20 000	10

^{*a*} Polymerization conditions: solvent = dry dioxane; ambient temperature; 2 h; amount of additive, 0.5 equiv; KtBuO added as a solid. ^{*b*} Purification: first for 2–12 h in dioxane at 98 °C; second in THF at 68 °C for 2 h. ^{*c*} Standard: general polymerization procedure in which no additives are used. ^{*d*} Number in parentheses: yield before purification in THF.

solution in an amount of 0.5 equiv, respectively. Base solutions were added via the septum using a glass syringe. After the standard reaction time of 2 h, the reaction mixtures were still mainly yellow. The temperature was raised to 98 °C for 2 h, and the homogeneous solution was then cooled to 40 °C. Addition of water did not result in precipitation for reaction with additives **9** and **10**, although for the latter an oily fraction was withheld by filtration. Filtrates were extracted with chloroform, and the combined organic layers were dried under reduced pressure.

Deprotonation Test on Additives 9, 10, and 11. To check if deprotonation occurs, the additives were dissolved in diethyl ether and repeatedly washed with an aqueous solution of NaOH. In the case of additives **9** and **10** the aqueous layer did color slightly pink; as could be expected, no coloration is visible in the case of additive **11**. TLC analyses of the organic layers after separation did reveal the presence of original products. These results indicated that additives **9** and **10** can be partly deprotonated in these basic conditions, while the di*tert*-butylated derivative cannot.

General Remarks and Instrumentation. ¹H NMR spectra were obtained in CDCl₃ at 300 or 400 MHz on a Varian Inova spectrometer using a 5 mm probe. Chemical shifts (δ) are expressed in ppm relative to the TMS absorption. All spectra were recorded at room temperature. Direct insert probe mass spectrometry (DIP-MS) analyses were carried out on a Finnigan TSQ 70, electron impact mode, mass range 35–550 and an interscan time of 2 s. The electron energy was 70 eV. Fourier transform infrared spectroscopy was performed on a Perkin-Elmer 1600 FT-IR (nominal resolution 2 cm⁻¹, summation of 16 scans). Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) with a narrow polydispersity by size exclusion chromatography (SEC). Separation to hydrodynamic volume was obtained using a Spectra series P100 (Spectra Physics) equipped with two mixed-B columns (10 μ m, 2 \times 30 cm \times 7.5 mm, Polymer Labs) and a refractive index (RI) detector (Shodex) at 40 °C. SEC samples were normally filtered through a 0.45 μm filter, but in the case of filtration problems, a 1.0 μ m filter was used. HPLC grade THF (p.a.) was used as the eluent at a constant flow rate of 1.0 mL/min. Toluene was used as flow rate marker. Thin-layer chromatography (TLC) was carried out on Merck precoated silica gel 60 F254 plates using chloroform as eluent.

Results and Discussion

A combination of additives (Figure 2) was chosen to respond to recent publications and clarify some claimed effects. Additive amounts of 0.5 equiv were used to enhance the visibility of effects. Additives **9**, **10**, and **11** were included in one of the final stages of the research, in response to a publication of Ferraris and co-workers.⁷ As a consequence, they are not used to the same extent in every section.

The precipitation procedure in methanol following polymerization resulted in a polymer fraction held by the filter and a residual fraction containing the methanolsoluble entities. The results listed in the tables under the title "standard" refer to the results of a general polymerization procedure in which no additives are used (for more details see the Experimental Section).

The Sulfinyl Route in THF. The additive effects were first studied in the sulfinyl route in THF (Table 1). Experiments were performed in duplicate and at random—to check for reproducibility and cancel possible time influences. All SEC analyses present a monomodal molecular weight distribution. All of the ¹H NMR spectra of the polymer fractions contain the same set of signals corresponding to OC_1C_{10} –PPV; end groups were not detected. However, a common feature of the ¹H NMR analyses of all residual fractions is the emergence of several minor signals in the region between 10.30 and 10.50 ppm—possibly originating from carbonyl and/or carboxyl groups.¹¹

Addition of 0.5 equiv of TEMPO completely inhibited polymer formation, indicating that radical processes occur. ¹H NMR analyses of the corresponding residual fractions demonstrate that a new, and most intense downfield signal emerges at 9.93 ppm. Signals at 7.81, 7.30, and 2.95 ppm and their integration values are consistent with the dialdehyde identified in earlier work.⁸ This dialdehyde originates from a derivative of the initiating dimer. When the residual monomer intensity is set at 100%, this product has a relative intensity of 20%, which is relatively high compared to other signals present.

The additive tert-butylbenzyl chloride (tBuPhCH2Cl) did not seem to exhibit a strong effect, contradicting the experience of Hsieh et al.⁶ and the occurrence of an anionic polymerization mechanism. The addition of carbon tetrabromine decreased the molecular weight of the polymer by almost a factor of 10; an expression of its activity as a chain transfer agent. At the same time problems with precipitation after elimination occurthe precipitate is oily instead of fibrous-resulting in very low yields of isolated polymer. The corresponding residual fractions are reddish-brown in color, and according to NMR analysis, still contain an amount of polymer. Possibly, the remaining additive or side products hinder precipitation of the polymer by methanol addition. In view of these carbon tetrabromine results, the effect of tert-butylbenzyl bromide (tBuPhCH2Br) can be attributed to a chain transfer effect caused by the carbon-bromine bond, rather than to an anionic influence. Addition of 0.5 equiv of 2-tert-butyl-4-methoxyphenol to the polymerization mixture results in a somewhat deviating reaction workup. Although the color of the reaction mixture, after the elimination procedure, is (only) slightly orange, addition of methanol does not result in precipitation. Only after evaporation of all solvent does addition of methanol result in a yelloworange solution containing a small amount of finely distributed red polymer particles, which can be recovered by filtration. Clearly, both yield and molecular weight of the polymer are seriously affected. Additive **10** probably acts just like TEMPO as a radical scavenger, but is somewhat less effective. In contrast with the CBr₄ experiments the ¹H NMR spectra of the corresponding residual fractions do not contain any residual polymer signals, thus confirming the low yields.

We conclude that the sulfinyl route proceeds by a radical polymerization mechanism, and yields high molecular weight polymer. Figure 3 proposes a set of elementary reactions for the radical polymerization. The exact nature of the termination reaction remains unclear, but the presence of low intensity carboxyl and/or carbonyl signals in NMR spectra indicate that oxidation occurs. We found no evidence for an anionic polymerization mechanism.

The Gilch Route in THF. A similar series of experiments on the Gilch route in THF showed irreproducibility, as was observed by others.¹² All of the polymers were purified by dissolution in THF at 68 °C and precipitation with methanol at 40 °C. This purification procedure brings polydispersities to a more acceptable level, and already improves reproducibility, but not satisfactory. The corresponding results after purification are listed in Table 2. All SEC analyses present a monomodal molecular weight distribution. For most of the polymer solutions filtration through a 0.45 μ m filter during sample preparation is (severely) hampered, indicating "microgel" formation.⁶

The poor reproducibility indicates that for some reason the Gilch route in THF is much more sensitive to reaction conditions than the sulfinyl route and limits the number of conclusions to be drawn. Only the complete inhibition of polymer formation by addition of 0.5 equiv of the radical scavenger TEMPO is striking and reproducible. As this is considered to be insufficient to comment on the nature of the polymerization mechanism of the Gilch route, a reliable system to investigate the effect of additives on the Gilch route toward OC_1C_{10} -PPV was developed.

The Gilch Route in Dioxane. (a) Scanning for a **Reproducible Polymerization Method.** In an attempt to obtain reproducible results using the Gilch route, the solvent was changed to dry 1,4-dioxane—the solvent used for the industrial manufacture of OC_1C_{10} — PPV—and several other parameters, like relative base quantities and temperature were evaluated.

(1) Variation of Base Conditions. According to the Covion publication¹¹ the use of dry dioxane as polymerization solvent is linked to working at elevated temperature (98 °C) under reflux and this is applied in this set of experiments. The effect of the change of solvent is tested respecting the base quantities of a standard procedure applied in previous sections: 1.3 equiv of potassium tert-butoxide (KtBuO) to initiate polymerization, followed by the addition of another 3.3 equiv of solid base to proceed with the conversion from the precursor stage to the conjugated polymer. Next, a variation in base addition is evaluated by applying the base quantities of the publication¹¹ (2.6 and 2.0 equiv of solid base for polymerization and elimination, respectively). Notice that the total amount of base added to the reaction mixture is kept constant in all experiments. All polymers are purified in THF at 68 °C prior to SEC analysis (Table 3), suppressing tailing on the low molecular weight side of the SEC-chromatogram (Figure 4) and lowering the polydispersity.

As is demonstrated by the results listed in Table 3 the transfer to another solvent can be regarded as a success: performing the Gilch route in dioxane at 98 °C leads to an improved reproducibility. However, the obtained yields are slightly lower compared to those of the industrial process (54% after purification), possibly due to a larger sensitivity to losses while working with relatively small quantities. Currently, the reason for the difference in reproducibility between the results obtained in THF and dioxane is still obscure. Changing the partial amounts of base added-the last two rowsdoes not seem to exhibit much of an effect. The corresponding deviations in molecular weight do not seem to be satisfactorily pronounced to determine a concentration effect, if any. As a consequence, the amounts of base, 1.3 and 3.3 equiv, are set as standard conditions for future experiments, even as the addition in solid state. In this way, a link with the Gilch experiments in THF as well as with the sulfinyl experiments is retained.

(2) Polymerizations at Ambient Temperature. Because the experiments in THF were performed at ambient temperature, the effect of this condition was checked on a Gilch polymerization in dioxane-hence temperature was lowered from 98 to about 25 °C. The corresponding results are listed in Table 4. During these polymerizations a new feature arose: within 1 h of reaction a phase separation was completed-an orangered colored lump of polymer was floating in a light orange solution. Further work up resulted in complete isolation of the crude lump, representing the major part of reaction products (yield = 94%). The corresponding characterization of its molecular weight distribution is listed in entry 1. During SEC sample preparation, difficulties with solubility and filtration were encountered, pointing at some gel properties of the lumpexplaining or resulting in the extremely high numbers for molecular weight and polydispersity. In an attempt to solve the problem of the phase separation and/or gelation, the lump of crude polymer was subjected to a

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purification treatment in THF at 68 °C. After a short while the contours of the lump began to fade, and some swelling was observed. A continuation of the treatment for over 72 h merely resulted in a minor dissolution of the lump; hence, a further continuation of the thermal treatment was considered to be inadequate. From the precipitated fraction a SEC sample was prepared, resulting in the values listed in the second entry. The molecular weight as well as the polydispersity is already somewhat lowered, but still the same filtration problems as with the previous sample are encountered.

Because the primary experiments conducted at elevated temperature did not yield any phase separation, dioxane was added once more to the polymer fraction and the mixture was brought at 98 °C for 2 h. In this relatively short time, the lump completely dissolved and an entirely homogeneous orange solution was obtained. This behavior is an indication that a physically crosslinked gel is involved. Cooling down does result in an increase in viscosity, however a phase separation no longer occurs. During SEC sample preparation, no significant problems with solubility or filtration are encountered. The corresponding results are displayed in the third entry of Table 4, and the SEC data show good correspondence with those of the experiments at elevated temperature (Table 3, first and second entry).

To check the observed influence of temperature another polymerization is performed at ambient temperature-again resulting in a phase separation-but this time the temperature is raised until 98 °C immediately after the standard reaction time of 2 h. In less than 12 h, a completely homogeneous orange solution is obtained and further work up is executed. A sample of the red fibrous polymer is analyzed with SEC-no problems were encountered during sample preparation-and the corresponding results are listed in the fourth entry. They already are in good agreement with the results displayed in entry 3. Nevertheless, the polymer fraction is subjected to purification in THF at 68 °C, but this does not alter much (entry 5). On the basis of these observations, it can be argued that a polymerization at ambient temperature in dioxane results in a physical network that can only be unraveled by a thermal treatment at a temperature of about 98 °C. This feature of phase separation/gelation is currently under evaluation and will be discussed in more detail in a future paper.

A close comparison with the experimental results obtained in dioxane at elevated temperature yields comparable molecular weight distributions. However, the ambient temperature experiments result in a significant higher yield (less side reactions) and therefore this room temperature is set as standard for further experiments in order to evaluate the influence of additives on the Gilch route.

(b) Results and Discussion of Additive Effects. To solve the feature of phase separation all polymers were subjected to a two-step purification procedure. A first step consists of the heating of the crude reaction mixture to 98 °C immediately after polymerization reaction until a homogeneous solution is obtained (2–12 h). After appropriate workup, the dried polymer fraction is subjected to a second, thermal treatment in THF at 68 °C for 2 h. As mentioned earlier, the latter procedure results quite often in a suppression of tailing on the low molecular weight side of the SEC chromatogram, leading to a lower polydispersity value of the

molecular weight distribution. To demonstrate this effect a selection of data prior to and after this second purification is listed in Table 5 in the even and odd numbered entries, respectively, and an overlay of the corresponding chromatograms of entries 3 and 4 is presented in Figure 4.

This thermal procedure gives rise to two distinct residual fractions: before and after purification in THF. ¹H NMR analysis of the former residual fraction only shows sharp signals of low molecular weight products, while the spectra of the latter residual fractions also contain broader polymer or oligomer signals, indicating that the treatment causes some polymer to stay in solution during the precipitation procedure. From now on, only the SEC results after the thermal treatment in THF will be listed, as evaluations are based upon these.

For all experiments, the amount of additive is set at 0.5 equiv to enhance the visibility of effects and maintain a link with previous experiments (sulfinyl and Gilch in THF). As response to the publication of Ferraris et al.⁷ additives **9** and **10** are included in the study. An overview of the obtained results confirms that the optimized polymerization procedure indeed shows an acceptable reproducibility (Table 6).

All polymer fraction ¹H NMR spectra are identical and in accordance with the structure of OC_1C_{10} -PPV. The complexity of the ¹H NMR spectra of the residual fractions does not allow a detailed characterization of side products. It is observed that monomer and additive signals are always present to some extent in these residual fractions. The low intensity signals neighboring the monomer peaks are probably originating from an oligomer fraction. Between 10.20 and 10.40 ppm several new minor signals emerge-possibly pointing at the presence of carbonyl and/or carboxyl groups. Only the residual fraction of the TEMPO experiment shows an additional signal around 9.7 ppm, possibly pointing at a dialdehyde structure. This could be originating from an initiating dimer,⁹ but its detailed structure could not be confirmed.

The standard polymerization procedure leads to polymer with a molecular weight from 700 000 to 800 000 in a yield exceeding 70% after purification. Addition of 4-tert-butylbenzyl chloride or bromide does not affect the polymer yield and resulted in a small decrease in molecular weight. It can be concluded that these additives-even in the relatively large amount of 0.5 equiv-do not exhibit the effect experienced by Hsieh et al. and do not act as anionic initiators or end caps for the polymerization. This is also confirmed by Andersson et al.¹³ The observed small decrease in molecular weight could, considering the effect of carbon tetrabromine, rather be interpreted as a chain transfer effect. The formation of stilbenes is confirmed by analysis of the residual fractions using mass spectrometry. The addition of carbon tetrabromine results in a serious decrease in molecular weight and a lowering of polydispersity, while the yield is not affected. This is consistent with it acting as a chain transfer agent. The effect of TEMPO on the polymerization is in accordance with the inhibition of a radical polymerization mechanism; the yield of polymer and the molecular weight both decreased by a factor of about 4. Possible reasons why polymerization is not completely inhibited are a second initiation of polymerization by addition of the second portion of base and a decreased efficiency of

additive	fraction	M _w (g/mol)	M _n (g/mol)	PD	yield (%)
reference ^a	$\mathbf{P}\mathbf{M}^d$	1 021 000	60 000	17	65
	PM	1 189 000	42 000	28	70
MeOPhOH ^b	all	63 600	30 500	2.1	2^c
	all	66 800	29 900	2.2	3 ^c
tBuMeOPhOH ^b	residual	50 400	21 600	2.3	2^c
	oily	2500	740	3.4	
	residual	41 300	17 300	2.4	3^c
	oily	1700	740	2.3	
di <i>t</i> BuMeOPhOH ^b	РŇ	47 600	18 100	2.6	8
	PM	51 000	18 900	2.7	10

^{*a*} Polymerization conditions: solvent = dry dioxane; ambient temperature; 2 h; no additives; KtBuO added as solution. Purification: first for 2-12 h in dioxane at 98 °C; second in THF at 68 °C. ^{*b*} Polymerization conditions: see footnote *a*, +0.5 equiv of additives. ^{*c*} These yields are estimated values, calculated from corresponding SEC chromatograms. ^{*d*} PM: polymer fraction.

TEMPO in the present conditions. To distinguish both possibilities, an additional experiment was set up in which a second amount of TEMPO (0.2 equiv) was added to the reaction mixture together with the second base portion. In this case, no polymer was found, supporting the idea of a second initiation. Corresponding ¹H NMR spectra similar to the other TEMPO experiments are found.

The effects of the additives 4-methoxyphenol, 9, and 2-tert-butyl-4-methoxyphenol, 10, are more complex. Reproducibility of molecular weight is poor-explaining the experiments in triplicate-whereas the yield after purification is somewhat more consistent. No phase separation occurred during polymerization, but the thermal treatment in dioxane and THF was nevertheless completed. Before purification, the resulting polymer was a wet, sticky substance-probably because side products are entrapped-which complicated separation, leading to a spread in yields. Apparently for these reactions the molecular weight of the resulting polymer is very sensitive to reaction conditions, leading to a large spread in molecular weights. The yields decreased to an extremely low level indicating a huge influence of these additives on the reactions occurring during synthesis. However, as the additive 2-tert-butyl-4-methoxyphenol (10), which has less nucleophilic properties, seems to exhibit a similar effect on the yield as additive 9, these results do not support the hypothesis of anionic initiation.

To approximate the conditions of Ferraris et al.⁷ somewhat more, additional experiments were set up in which the additives **9** and **10** were added together with the base as solution, increasing the probability of them acting as nucleophile or base. Additive 11 is included in the study to obtain additional information on the nature of the effects. If all three additives exhibit a comparable effect on the polymerization, a radical polymerization process is more likely than an anionic. On the contrary, when large differences in effects of the distinct additives are obtained, this does present an important indication in favor of anionic processes. To have some reference values two polymerizations (without additives) are performed in which the base is added as solution (in amounts of 1.3 and 3.3 equiv). The corresponding results are listed in entries 1 and 2 of Table 7. It can be concluded that the polymerizations in which the base is added as solution yield a somewhat

higher weight-average molecular weight (M_w) value and an increased polydispersity in comparison to reactions where the base is added as a solid (Table 3, entries 1 and 2).

During the polymerization reactions with these additives 9, 10, and 11 no phase separation occurs, even if the base amounts are adjusted to 2.6 and 2.0 equiv to enhance the probability of polymerization. The reaction mixtures do not color a deep orange, but remain yellow to slightly orange for 9 and 10, and light orange in the case of **11**. The result of the precipitation procedure is dependent on the additive used and will therefore be discussed separately. In the case of the reaction with 4-methoxyphenol (9), no polymer precipitates; hence, an extraction is performed leading to one yellow-orange fraction containing all organic products formed. For this reason, in Table 7, it is referred to as fraction "all" . Precipitation of the reaction mixture resulting from addition of 2-tert-butyl-4-methoxyphenol (10) yields some kind of reddish "oily" fraction, instead of fibers, which can be recovered by filtration. The remains of the reaction mixture is subjected to further workup consisting of extraction and drying under reduced pressure (precipitation does not yield any polymer). This yelloworange fraction is referred to as the "residual" fraction. Polymerization in the presence of 2,6-di-tert-butyl-4methoxyphenol (11) does yield an orange reaction mixture. By precipitation in water and neutralization, a small amount of red polymer ("PM" fraction) separates from the solution. However, this polymer turns out to be unmanageable, complicating its recovery by filtration. It easily spreads out over a large surface and is very hard to remove although addition of methanol somewhat facilitates collection (similar to the previous experiments with carbon tetrabromine on the sulfinyl route toward OC₁C₁₀-PPV). Although no explicit polymer could be separated in the case of additives 9 and **10**, SEC samples from each fraction are nevertheless prepared and analyzed. These analyses detect the presence of a higher molecular weight species, however, an important remark is that the detector response for these samples is extremely low. This is in accordance with the NMR spectra, where at first no polymer signals could be detected, pointing at very low corresponding concentrations and hence low yields. In the case of polymerizations in the presence of 9 and 10, the yield is calculated taking relative peak areas in the corresponding chromatograms together with relative amounts of the fractions (e.g., the ratio residual over oily fraction) into account. Although other monomer signals-including those of the alkoxy side chains-are present, none of the other spectra seem to contain remaining PhCH₂Cl signals. The residual fraction resulting from the experiments with 10 do not seem to vary much from the spectra of the corresponding oily fractions. Additive signals all are present except for the hydroxide signal, which is possibly hidden below other signals or its disappearance indicates the formation of an adduct structure. However, due to an overcrowding of the NMR spectra between 2.5 and 4.2 ppm, the identification of such adduct structure is hampered. New intense signals emerge between 5.8 and 7.0 ppm, but currently no reasonable explanation can be offered for this feature.

Although the various fractions that contain polymer to a certain extent behave differently, it can be stated that the effect of the three additives is comparable. They all result in a substantial decrease in yield together with a significant lowering of molecular weight, pointing at a similar interference in reactions. In combination with the other results reported, it can be concluded that their main effect is a strong radical inhibiting one, as described previously for the case of quinones.¹⁴ This strongly supports the hypothesis of a radical mechanism.

As a whole, the results of the experiments on the Gilch route in dioxane present a strong indication that the main polymerization mechanism of the Gilch route is radical in nature and yields high molecular weight polymer.

Conclusions

This study was undertaken in an attempt to elucidate the nature of the polymerization mechanism—anionic or radical—of *p*-quinodimethane-based polymerizations. A combination of additives was used to investigate the polymerization mechanism by looking at their influence on the reaction and its products.

First of all, the effect of the additives was studied on the sulfinyl route in THF toward OC₁C₁₀-PPV. One of the most striking observations is the result of the TEMPO experiments: this addition leads to a complete inhibition of polymer formation, presenting a strong indication that radical processes occur. The additive tertbutylbenzyl chloride does not seem to exhibit a strong effect, if any. Carbon tetrabromine and tert-butylbenzyl bromine affect the molecular weight just like a chain transfer agent would (except for the lowering of the yield in the case of the former). It can be stated that these results lie in the line of expectation elaborated in previous mechanistic studies on the sulfinyl route and present strong indications that in these experimental conditions a radical polymerization mechanism is involved that yields high molecular weight polymer.

The complexity of the NMR spectra of experiments with additives on the Gilch route clearly indicates that this route is even more complex and presents new problems to solve. The Gilch route in THF is demonstrated to yield irreproducible results, which invites some questions on the conclusions of some publications of others. Perhaps a reexamination and/or reinterpretation of the results are required. As a consequence of the poor reproducibility of results in THF, the solvent was changed to dioxane. A reproducible polymerization procedure to synthesize OC_1C_{10} -PPV via the Gilch route at room temperature was developed, based on the industrial procedure, and used to investigate the influence of the various additives.

Compared to the sulfinyl route, the Gilch route is clearly more sensitive to reaction conditions, but similar conclusions can be drawn. Addition of TEMPO can completely inhibit polymer formation by its function of radical scavenger. Carbon tetrabromine acted as chain transfer agent: molecular weight decreased while the yield was left unchanged. The small decrease in molecular weight by the additives 4-tert-butylbenzyl chloride and bromide can in this view also be interpreted as a chain transfer effect. No indications are found for them acting as anionic initiators or end-caps for the polymerization, contradicting findings of other research groups. Primary experiments with distinct methoxyphenols, to elucidate the effect of the nonsubstituted derivative, led to a poor reproducibility of molecular weights. In additional experiments the various p-methoxyphenols were added together with the base as solution, approximating the conditions of other publications somewhat more. All three additives result in a substantial decrease in polymer yield together with a significant lowering of molecular weight. This points to a similar radical inhibiting interference in the reactions and strongly refutes the anionic assertion claimed by others.

Taken as a whole, all results support the argument that also the main polymerization mechanism operating in the Gilch route is radical in nature, yielding high molecular weight polymers, as is the case for the sulfinyl route. Moreover, the results obtained are inconsistent with an anionic polymerization mechanism and invite some questions on the conclusions of others.

This knowledge of the nature of the polymerization mechanism offers potential for an enhanced control on the reaction processes and product handling and hence on the molecular weight and structure of the resulting polymer.

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