

The synthesis of poly(4,4'-biphenylene vinylene) and poly(2,6-naphthalene vinylene) via a radical chain polymerisation

M. Van Der Borgh, P. Adriaensens, D. Vanderzande*, J. Gelan

Laboratory for Organic and Polymer Chemistry, Limburg University, Institute for Material Research, Division Chemistry, University Campus, B-3590 Diepenbeek, Belgium

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Abstract

Chain polymerisations used for the synthesis of poly(arylene vinylene)s have in common that they proceed via a quinoid compound. The formation of this compound is a high-energy step that involves the loss of the aromatic resonance energy of the monomer and hence must be compensated by a driving force. In order to comprehend this driving force monomers with a growing aromatic resonance energy are polymerised via the sulphanyl precursor route described. Next the conversion of the synthesised polymers to their corresponding conjugated polymer is followed with different techniques and the u.v.–vis. absorbance and photoluminescence spectra are determined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(arylene vinylene)s; Driving force; Blue–green photoluminescence

1. Introduction

Since the discovery of electroluminescent properties of poly(*p*-phenylene vinylene) (PPV) derivatives worldwide there has been an intense research on this topic [1–3]. At this moment the luminescence and lifetime of Polymer Light Emitting Diodes (PLEDs) emitting in the red and the green part of the visible spectrum, are sufficient to be competitive with the classic inorganic LEDs. Only the fabrication of highly efficient PLEDs with a blue emission is still a problem.

The synthesis of the PPV-type polymers can be divided into two major approaches, the direct synthesis of conjugated polymers, and the indirect methods, the so-called precursor routes. These direct routes are step polymerisations, which deliver double bonds between the aromatic rings immediately after synthesis. The consequence of this method is the formation of rigid and insoluble polymers, unless only oligomers are formed or long flexible alkyl chains are placed on the polymer [4–15].

The different chain polymerisations used for the synthesis of poly(arylene vinylene) derivatives have in common that they proceed via a *p*-quinodimethane (q.m.) derivative, which is formed in situ, and polymerises spontaneously [16–23]. In our laboratory we have tried to fit the common

features of these chain polymerisations into one general scheme. Out of this scheme a new route has grown [24–26]. The monomers in this route possess a leaving group and a so-called polariser, which differs from the former. This distinction is one of the main differences between our precursor route and the other routes known from literature for the synthesis of conjugated polymers. An important advantage of our method is the possibility to choose the polariser, leaving group, base and solvent as a function of the monomer, which must be polymerised. It was shown by us that the use of a *n*-alkylsulphanyl group as polariser and a halogen as leaving group leads to stable and soluble precursor polymers (see Fig. 1).

The 1,6-elimination reaction to form the q.m. system, which in fact is the actual monomer for the polymerisation, is a high-energy step that involves the loss of resonance energy of the aromatic system. Hence a driving force for the q.m. formation is required. In order to reveal this driving force, the 1,4-phenyl, 2,6-naphthyl and 4,4'-biphenyl derivatives of our monomers are proper structures as they possess an increasing resonance energy in their π -systems. It is even so that, to our knowledge, up to the present no work is published describing the chain polymerisation of monomers possessing a high aromatic resonance energy, like the 4,4'-biphenyl or 2,6-naphthalene derivatives. Indeed, the loss of resonance energy coupled with the q.m. formation imposes a limitation on the type of monomers that can be polymerised as a function of the arylene

* Corresponding author. Tel.: +32-11-268321; fax: +32-11-268301.

E-mail address: dvanderz@luc.ac.be (D. Vanderzande).

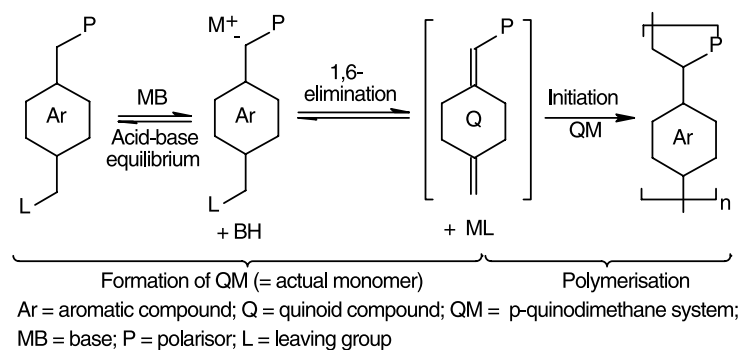


Fig. 1. General scheme for the synthesis of poly(arylene vinylene)s.

moiety. As a consequence it is not possible to polymerise the 2,6-naphthalene and 4,4'-biphenyl derivatives via the Wessling route [19]. Until now, one only succeeded in the synthesis of poly(4,4'-biphenylene vinylene) and poly(2,6-naphthalene vinylene) derivatives via stepwise polymerisation methods [8,27,28]. They deliver polymers with rather low molecular weights, which is inherent to these routes. On the contrary, poly(1,4-naphthalene vinylene) can be synthesised via the Wessling precursor route, because of the similar loss of resonance energy compared to the 1,4-phenylene derivatives, on formation of the 1,4-naphthalene-*p*-quinodimethane system [20].

Another motivation for the choice of this work is the expectation that the use of these structures as the aromatic part in poly(arylene vinylene)s causes a blue shift in their photo and electroluminescence. This way it may be possible to synthesise a conjugated polymer that can be used as the electroluminescent layer in highly efficient blue PLEDs.

The aim of this paper is to answer three questions. Firstly, is it possible to polymerise derivatives possessing extended aromatic structures, like the 2,6-naphthyl and 4,4'-biphenyl derivatives? Secondly, what is the driving force necessary for the q.m. formation and how can it be controlled? And thirdly, do these precursor polymers so obtained lead to conjugated polymers luminescent in the blue region of the visible spectrum?

2. Experimental

Materials. All solvents and reagents are purchased from ACROS or Aldrich except NaOH (VEL). All these materials are reagent grade and are used without further purification unless otherwise noted. Chromatographic separations were performed on Macherey–Nagel silica gel (particle size: 0.023–0.2 mm). Thin layer chromatography was performed on Merck silica gel 60F₂₅₄. The syntheses and characterisations of **4d–e**, **5d–e** [29], **6d–e** [30] and **7c** [25] are already described elsewhere.

Analyses. Melting points are measured on a Buchi 510. Mass spectra were determined on a Finnigan MAT TQ70 (electron energy: 70 eV). ¹³C n.m.r. spectra were recorded

on a Varian Spectrometer at 100 MHz and ¹H n.m.r. spectra at 400 MHz. Chemical shift assignments are given in ppm relative to internal TMS as standard. Infrared spectroscopy was performed on a Philips Pye Unicam SP-3000 i.r. or a Perkin–Elmer 1600 f.t.-i.r.. Size exclusion chromatography (s.e.c.) analyses of the polymers are performed at 70°C with flow rates of 1.0 ml/min in DMF using a differential refractometer detector (Shodex) and two MIXED-B (10 μm, 2 × 30 cm²) columns (Polymer Labs) after calibration with polystyrene standards (Polymer Labs). The glass transition temperatures (*T*_g) were determined on a modulated differential scanning calorimeter (TA Instruments 2000; He flow, 30 ml; heating rate, 2.5°C/min; amplitude, 1.5°C; period, 60 s; temperature calibration with In and benzophenone; *C*_p calibration with a PMMA NIST standard, closed Al pans). The precursor polymers were converted in a SHEL-LAB 1410D vacuum oven (vacuum: 5 mbar) or a CARBO-LITE Cascade Controlled (LAB69301) Furnace (11/96/2945) (vacuum: 0.5 mbar). The vacuum was obtained with a Leybold DB4 pump. Thermogravimetric analyses are carried out on a Dupont Instruments 951 Thermo Gravimetric Analyser (N₂ flow, 50 ml; heating rate, 10°C/min). U.v.–vis.–spectra were recorded on a DW-2000TM u.v.–vis. Spectrophotometer or a Shimadzu UV-1602 u.v.–vis. Spectrophotometer. Photoluminescence spectra were determined on a Perkin–Elmer LS-5B Luminescence Spectrometer.

4,4'-Di(methylhydroxy)biphenyl 2a. In a 1250 ml three-necked flask fitted with an efficient condenser, a thermometer and a dropping funnel is placed a suspension of 6.2 g LiAlH₄ (0.144 mol) in 80 ml dry THF under an inert atmosphere. The dropping funnel is placed between the condenser and the flask and is equipped with a pressure-equalising tube and a sintered glass instead of a vessel. 30 g (0.122 mol) of **1a** is placed on the sintered glass in the funnel. The mixture is refluxed with stirring until **1a** is added in solution through the sintered glass to the reaction mixture. Then the reaction mixture is refluxed for another hour. The mixture is cooled to –20°C and 80 ml of H₂O is added drop by drop, followed by a slow addition of 80 ml of 20% H₂SO₄ (aq). Next the THF is evaporated under reduced pressure to give a suspension of white product in water.

The product is filtered and washed with H₂O. After recrystallisation from acetone, white crystals are obtained. 93% yield [31]; m.p. 187.3–188.5°C; i.r. (KBr, ν , cm⁻¹): 3300, 2910–2820, 1485, 1380, 1030–1000, 820, 790; ¹H n.m.r. (acetone-d₆, 400 MHz): 7.62 (d, ³J = 8.20 Hz, 4H), 7.45 (d, ³J = 8.20 Hz, 4H), 4.67 (s, 4H); m.s. (E.I., *m/z*, relative intensity in %): 214 (M⁺, 100), 197 (M⁺–OH, 13), 183 (M⁺–CH₂OH, 20), 167 (M⁺–CH₂OH–OH, 20), 153 (M⁺–2 CH₂OH, 24), 107 (M⁺–phenyl–CH₂OH–H, 107), 91 (M⁺–phenyl–CH₂OH–OH, 5), 77 (M⁺–phenyl–CH₂OH–CH₂OH, 20).

2,6-Di(hydroxymethyl)naphthalene 2b. For the synthesis of **2b** the same procedure is used as described for the synthesis of **2a**. After recrystallisation from acetone, white crystals are obtained. About 90% yield[31]; m.p. degradation starts at about 180°C, at 400°C a dark brown product is obtained which doesn't melt; f.t.-i.r. (KBr, ν , cm⁻¹): 3236, 2914, 2867, 1443, 1406, 1209, 1160, 1128, 1029, 895, 821, 707, 486; ¹H n.m.r. (acetone-d₆, 400 MHz): 7.83 (d, ³J = 8.42 Hz, 2H), 7.82 (s, 2H), 7.49 (d, ³J = 8.42 Hz, 2H), 4.78 (s, 4H); m.s. (e.i., *m/z*, relative intensity in %): 188 (M⁺, 89), 171 (M⁺–OH, 7), 157 (M⁺–CH₂OH, 31), 141 (M⁺–CH₂OH–OH, 22), 129 (M⁺–2 CH₂OH, 100).

4,4'-Di(chloromethyl)biphenyl 3a. In a 50 ml flask fitted with a condenser is placed 1 g (0.005 mol) of **2a** and 2 g ZnCl₂ (0.015 mol). 17 ml HCl (conc.) is added while the reaction mixture is stirred. The reaction mixture is refluxed for 4 h and then poured into 200 ml H₂O. The white product is filtered, dissolved in CHCl₃ and washed with water. The organic layer is dried (MgSO₄) and evaporated under reduced pressure. The product is purified by column chromatography (silica, CHCl₃) and recrystallised from hexane to give white crystals. About 83% [32] yield; m.p. 140.2–141.4°C; i.r. (KBr, ν , cm⁻¹): 3000, 2920, 1480, 1430, 1385, 1255, 1000, 810, 720, 670, 550, 470; ¹H n.m.r. (CDCl₃, 400 MHz): 7.56 (d, ³J = 8.28 Hz, 4H), 7.45 (d, ³J = 8.28 Hz, 4H), 4.62 (s, 4H); m.s. (e.i., *m/z*, relative intensity in %): 250 (M⁺, 100), 215 (M⁺–Cl, 86), 181 (M⁺–2 Cl, 62), 152 (M⁺–2 CH₂Cl, 12), 90 (M⁺–Cl–phenyl–CH₂Cl, 3), 76 (M⁺–CH₂Cl–phenyl–CH₂Cl, 29).

2,6-Di(chloromethyl)naphthalene 3b. For the synthesis of **3b** the same procedure is used as described for the synthesis of **3a**. The product is purified by recrystallisation from toluene to give white crystals. About 85% yield [32]; m.p. 143.8–146.4°C (lit. 140.0–143.0)[20]; f.t.- i.r. (KBr, ν , cm⁻¹): 2960, 1494, 1442, 1398, 1274, 1119, 825, 728–678, 564, 485; ¹H n.m.r. (CDCl₃, 400 MHz): 7.82 (d, ³J = 8.40 Hz, 2H), 7.81 (s, 2H), 7.51 (d, ³J = 8.40 Hz, 2H), 4.73 (s, 4H); m.s. (e.i., *m/z*, relative intensity in %): 224 (M⁺, 31), 189 (M⁺–Cl, 100), 154 (M⁺–2 Cl, 33), 128 (M⁺–2 CH₂Cl, 3).

4-Chloromethyl-4'-(n-butylsulphanyl)methylbiphenyl 4a. About 15 g (0.06 mol) of **3a** is dissolved in 105 ml toluene. 6.3 g (0.157 mol) NaOH dissolved in 105 ml H₂O is added together with 0.26 g of a phase transfer catalyst, Aliquot 336. To this solution a mixture of 3.2 ml (0.029 mol) *n*-buta-

nethiol dissolved in 32 ml toluene is added drop by drop. When this solution is added completely, the mixture is stirred for another hour. The organic layer is separated, washed with water, dried over MgSO₄, filtered and evaporated on a rotary evaporator to give a white product. **3a** is separated from the mixture obtained by means of a recrystallisation from CHCl₃/hexane (1/9). The filtrate is evaporated on a rotary evaporator to give an oil which consisted of the thioether **4a** and some residual **3a**.

4-Chloromethyl-4'-(n-octylsulphanyl)methylbiphenyl 4b and 2-chloromethyl-6-(n-octylsulphanyl)methylnaphthalene 4c. For the synthesis of **4b** and **4c** the same circumstances and concentrations are used as were described for the synthesis of **4a**.

4-Chloromethyl-4'-(n-butylsulphanyl)methylbiphenyl 5a. About 0.49 g (0.003 mol) TeO₂ is added to a solution of the partially purified **4a** in 180 ml MeOH. Under stirring 7 ml (0.062 mol) of a H₂O₂ solution (35 wt% in water) is added drop by drop. The mixture is stirred at room temperature until a slight over-oxidation to the sulphon appears on TLC. The reaction is quenched by adding 150 ml of a saturated NaCl solution. The water layer is extracted with CHCl₃. The combined organic layers are dried over MgSO₄, filtered and evaporated on a rotary evaporator to give white crystals. The different products are separated by column chromatography (silica, CHCl₃) to give pure white crystals of **5a**. 50% yield (relative to the *n*-butylthiol used for the synthesis of **4a**); m.p. 175.5–176.1°C; f.t.-i.r. (KBr, ν , cm⁻¹): 2955, 2923, 2858, 1496, 1400, 1268, 1023, 831, 730, 671, 490; ¹H n.m.r. (CDCl₃, 400 MHz): 7.57 (d, ³J = 8.22 Hz, 2H), 7.56 (d, ³J = 8.22 Hz, 2H), 7.45 (d, ³J = 8.22 Hz, 2H), 7.35 (d, ³J = 8.22 Hz, 2H), 4.01 (d, ²J = 13.00 Hz, 1H), 3.97 (d, ²J = 13.00 Hz, 1H), 2.60 (t, ³J = 7.57 Hz, 2H), 1.73 (m, 2H), 1.45 (m, 2H), 0.92 (t, ³J = 7.30 Hz, 3H); ¹³C n.m.r. (CDCl₃, 100 MHz): 140.42, 140.35, 136.67, 130.45, 129.15, 129.06, 127.49, 127.30, 57.64, 50.64, 45.87, 24.38, 21.95, 13.61; m.s. (e.i., *m/z*, relative intensity in %): 304 (M⁺–O, 1), 285 (M⁺–Cl, 1), 269 (M⁺–O–Cl, 87), 215 (M⁺–S(O)-*n*-Bu, 94), 195 (M⁺–phenyl–CH₂Cl, 17), 180 (M⁺–Cl–S(O)-*n*-Bu, 100), 152 (M⁺–CH₂S(O)-*n*-Bu–CH₂Cl, 8), 90 (M⁺–phenyl–CH₂S(O)-*n*-Bu, 4).

4-Chloromethyl-4'-(n-octylsulphanyl)methylbiphenyl 5b. About 1.13 g TeO₂ (7.11 mmol) is added to a solution of the partially purified **4b** in a mixture of 40 ml dioxane and 250 ml methanol. 15.8 ml (0.138 mol) of a H₂O₂ solution (35% in water) is added to the solution. After column chromatography **5b** is recrystallised from toluene. 40% yield (relative to the *n*-octanethiol used for the synthesis of **4b**); m.p. 161.5–162.9°C; f.t.-i.r. (KBr, ν , cm⁻¹): 2956, 2916, 2848, 1496, 1467, 1400, 1025, 830, 732, 673; ¹H n.m.r. (CDCl₃, 400 MHz): 7.57 (d, ³J = 8.22 Hz, 2H), 7.55 (d, ³J = 8.22 Hz, 2H), 7.44 (d, ³J = 8.22 Hz, 2H), 7.35 (d, ³J = 8.22 Hz, 2H), 4.61 (s, 2H), 4.02 (d, ²J = 12.80 Hz, 1H), 3.97 (d, ²J = 12.80 Hz, 1H), 2.61 (m, 2H), 1.74 (m, 2H), 1.39 (m, 2H), 1.25 (m, 8H), 0.84 (t, ³J = 7.05 Hz, 3H);

Table 1
Polymerisation results of **5a**

Solvent	Eq. base	T (°C)	High molecular weight			Low molecular weight		
			$\bar{M}_w (\times 10^4)$	D	Yield (%)	$\bar{M}_w (\times 10^4)$	D	Yield (%)
<i>t</i> -Butanol/CH ₂ Cl ₂	1.3	25	0.0	0.0	0	0.0	0.0	0
<i>s</i> -Butanol	1.3	20	0.0	0.0	0	0.0	0.0	0
MMF/CH ₂ Cl ₂ (1/1)	1.3	20	0.0	0.0	0	0.0	0.0	0
MMF	1.3	20	0.0	0.0	0	0.0	0.0	0
CH ₂ Cl ₂	1.3	20	7.3	2.3	10	0.0	0.0	0
NMP	1.3	-10	5.6	1.8	33	0.4	1.1	9
DMSO/THF (1/1)	1.3	20	4.9	2.1	45	0.9	1.6	10

¹³C n.m.r. (CDCl₃, 100 MHz): 140.37, 140.32, 136.64, 130.41, 129.14, 129.01, 127.45, 127.25, 57.63, 50.95, 45.84, 31.59, 29.03, 28.87, 28.71, 22.47, 22.39, 13.96; m.s. (e.i., *m/z*, relative intensity in %): 360 (M⁺-O, 1), 341 (M⁺-Cl, 1), 215 (M⁺-S(O)-*n*-Oct, 100), 180 (M⁺-Cl-S(O)-*n*-Oct, 29), 152 (M⁺-CH₂Cl-CH₂S(O)-*n*-Oct, 3).

2-Chloromethyl-6-(*n*-octylsulphanyl)methylnaphthalene 5c. For the synthesis of **5c** the same circumstances and concentrations are used as were described for the synthesis of **5a**. **5c** is purified by column chromatography (silica, CHCl₃) and recrystallised from toluene to give white crystals. 33% yield (relative to the *n*-octylthiol used for the synthesis of **4c**); m.p. 133.2–134.7°C; f.t.-i.r. (KBr, ν , cm⁻¹): 2954, 2922, 2849, 1496, 1266, 1027, 902, 834, 708, 480; ¹H n.m.r. (CDCl₃, 400 MHz): 7.73 (d, ³*J* = 8.49 Hz, 2H), 7.72 (s, 1H), 7.68 (s, 1H), 7.43 (d, ³*J* = 8.49 Hz, 1H), 7.34 (d, ³*J* = 8.49 Hz, 1H), 4.66 (s, 2H), 4.19 (d, ²*J* = 13.00 Hz, 1H), 4.10 (d, ²*J* = 13.00 Hz, 1H), 2.53 (m, 2H), 1.68 (m, 2H), 1.31 (m, 2H), 1.18 (m, 8H), 0.81 (t, ³*J* = 6.94 Hz, 3H); ¹³C n.m.r. (CDCl₃, 100 MHz): 135.12, 132.67, 132.36, 128.80, 128.46, 128.34, 128.11, 127.80, 127.05, 126.64, 58.06, 50.87, 46.14, 31.39, 28.84, 28.67, 28.49, 22.30, 22.20, 13.82; m.s. (e.i., *m/z*, relative intensity in %): 350 (M⁺, 1), 334 (M⁺-O, 1), 315 (M⁺-Cl, 1), 299 (M⁺-O-Cl, 1), 189 (M⁺-S(O)-*n*-Oct, 100), 154 (M⁺-S(O)-*n*-Oct, -Cl, 22).

Standard procedure for polymerisation. About 1 mmol of **5a–c** is dissolved in 10 ml solvent. This solution is flushed with N₂ under vigorous stirring for 1 h and a Na⁺tBuO⁻ solution is added. The polymerisation is allowed to proceed for 1 h under a constant stream of N₂. Then the reaction mixture is poured into 100 ml H₂O and neutralised with a

0.1 M HCl solution. The suspension is extracted twice with 100 ml CHCl₃. The organic layers are separated from the water layer, combined and evaporated under reduced pressure. The polymer is dissolved in 10 ml CHCl₃ and precipitated in the proper non-solvent mixture, filtered and dried under vacuum. All the solvents, the equivalents base and the reaction temperature used, are displayed in Tables 1–3 together with the yields and molecular weights of the polymers obtained. If CH₂Cl₂ is used as solvent, the base is added in solid state. When volatile solvents are used (THF, CH₂Cl₂) the vapours are trapped in a condenser placed on the reaction flask.

*Poly{[4,4'-biphenylene]-[1-(*n*-butylsulphanyl)ethylene]}* **6a.** The solvents used are, together with the amount of base and temperature, shown in Table 1. The polymers synthesised are precipitated successively in ether/THF (9/1) and ether/THF (7/3) to separate the monomer and the high and low molecular weight fraction. T_g 89°C; f.t.-i.r. (KBr, ν , cm⁻¹): 3445, 2957, 2929, 2870, 1681, 1494, 1463, 1401, 1034, 818; ¹H n.m.r. (CDCl₃, 400 MHz): 7.49, 7.36, 7.30, 7.14, 7.04 (8H), 3.98, 3.88, 3.75, 3.63, 3.39, 3.22, 2.97 (3H), 2.60, 2.41, 2.18 (2H), 1.69, 1.56 (2H), 1.29 (2H), 0.81 (3H); ¹³C n.m.r. (CDCl₃, 100 MHz): 140.78, 140.46, 138.20, 137.09, 132.87, 131.96, 130.29, 129.64, 129.50, 128.99, 128.85, 127.24, 126.96, 126.87, 126.79, 126.65, 70.01, 65.47, 50.48, 49.44, 48.90, 37.26, 36.12, 35.65, 24.66, 24.31, 21.89, 21.72, 13.50.

*Poly{[4,4'-biphenylene]-[1-(*n*-octylsulphanyl)ethylene]}* **6b.** The used solvents, amount of base, temperature, TEMPO, and water are shown in Table 3. The polymer was precipitated in a mixture of ether and THF (9/1). T_g 82°C; f.t.-i.r. (KBr, ν , cm⁻¹): 3444, 2955, 2926, 2855,

Table 2
Polymerisation results of **5b**

Solvent	# Eq base	Temperature (°C)	$\bar{M}_w (\times 10^4)$	D	Yield (%)
NMP	1.3	35 ^a	2.1	1.9	25
NMP + 5% H ₂ O	1.3	40 ^a	4.0	1.5	2
NMP + 0.5 eq TEMPO	1.3	35 ^a	0.8	1.1	5
CH ₂ Cl ₂	1.3	20	2.3	1.4	10
CH ₂ Cl ₂ + 0.5 eq TEMPO	1.3	20	0.9	1.4	1

^a The temperature is increased because of the low solubility of monomer **5b**.

Table 3
Polymerisation results of **5c**

Solvent	Eq Base	T (°C)	High molecular weight			Low molecular weight		
			$\bar{M}_w (\times 10^4)$	D	Yield (%)	$\bar{M}_w (\times 10^4)$	D	Yield (%)
MMF/CH ₂ Cl ₂ (1/1)	1.3	20	20.5	1.9	5	0.0	0.0	0
<i>s</i> -Butanol/CH ₂ Cl ₂	1.3	20	17.8	1.6	15	0.0	0.0	0
<i>s</i> -Butanol	1.3	60	14.9	1.7	20	0.0	0.0	0
THF	1.1	25	32.7	2.6	55	0.0	0.0	0
CH ₂ Cl ₂	1.3	20	36.8	2.4	55	0.0	0.0	0
NMP	1.3	20	16.5	3.7	30	0.9	1.2	5
DMSO/THF (1/1)	1.0	20	24.5	5.2	45	1.0	1.3	10

1682, 1497, 1464, 1402, 1043, 819, 753; ¹H n.m.r. (CDCl₃, 400 MHz): 7.49, 7.35, 7.29, 7.14, 7.05 (8H), 3.97, 3.88, 3.75, 3.61, 3.36, 3.21, 2.96 (3H), 2.57, 2.83, 2.16 (2H), 1.68, 1.57 (2H), 1.60 (10H), 0.79 (3H); ¹³C n.m.r. (CDCl₃, 100 MHz): 141.51, 141.18, 139.27, 138.88, 138.55, 137.79, 137.55, 133.61, 132.64, 130.99, 130.37, 129.71, 127.96, 127.58, 70.79, 66.21, 50.52, 49.97, 38.01, 36.88, 36.45, 32.20, 29.60, 29.47, 29.19, 23.59, 23.11, 14.63.

Poly{[2,6-naphthalene]-[1-(*n*-octylsulphanyl)ethylene]} **6c**. The solvents, amount of base and temperature used are shown in Table 3. The polymer synthesised was precipitated in ether/THF (9/1) and ether/THF (7/3) to separate the monomers and the high and low molecular weight fractions. *T*_g 81°C; f.t.-i.r. (KBr, ν , cm⁻¹): 3050, 2963, 2924, 2853, 1503, 1042, 890, 818, 479; ¹H n.m.r. (CDCl₃, 400 MHz): 7.71, 7.63, 7.57, 7.47, 7.38, 7.15, 7.05 (6 H), 4.02, 3.93, 3.41, 3.09 (3 H), 2.13, 2.37 (2 H), 1.53, 1.65 (2 H), 1.13 (10 H), 0.79 (3H); ¹³C n.m.r. (CDCl₃, 100 MHz): 136.30, 133.09, 133.02, 132.11, 132.94, 131.94, 131.77, 131.54, 131.33, 130.51, 129.61, 128.64, 128.09, 127.84, 127.69, 126.84, 126.10, 70.55, 65.81, 49.82, 49.19, 36.88, 36.80, 31.53, 28.97, 28.79, 28.54, 22.99, 22.45, 13.98.

*Procedure for monitoring the biphenyl-*p*-quinodimethane concentration by means of u.v.-vis. measurements.*

To a quartz cell with an internal cell length of 10 mm, 2 ml of a 0.025 M solution of **5b** in NMP and a magnetic stirrer are added. Whilst the monomer solution is stirred, 1 ml of a Na⁺tBuO⁻ solution in MMF (1.3 equivalents with respect

to **5b**) is added. The valve is closed and the measurement started.

Procedure for the conversion to the conjugated polymers. The precursor polymer is dissolved in the appropriate solvent (CH₂Cl₂, CHCl₃, dichlorobenzene, *sec*-butanol) and applied to a substrate by means of a spin coater (polymer conc.: 0.01 mg/ml, spinning rate: 1500 rpm, spinning time: 30 s) or by dripping of a polymer solution. Next the polymer is placed under vacuum into an oven. When the vacuum oven is used, the substrate is placed directly into the oven. In the Carbolite oven, the substrate is placed in a glass tube that is placed under vacuum. For the u.v.-vis.-absorption and photoluminescence measurements quartz substrates were used, for the i.r.-absorbance measurements, KBr-substrates.

Poly(4,4'-biphenylene vinylene) 7a. f.t.-i.r. (KBr, ν , cm⁻¹): 3025, 1498, 964, 818.

Poly(2,6-naphthalene vinylene) 7b. f.t.-i.r. (KBr, ν , cm⁻¹): 3021, 1600, 1500, 958, 888, 814.

3. Results and discussion

3.1. Driving force for the q.m. formation and synthesis of the precursor polymers

The global reaction formulated for the formation of the q.m. system can be splitted into two major parts, the formation of the q.m. system and two acid–base equilibria (Fig. 2). The former part must be strongly endergonic ($\Delta G_{\text{elim(gas)}}^0 > 0$ or $K_{\text{elim(gas)}} < 1$) as the resonance energy of the benzene structure is lost. In order to have an exergonic global process ($\Delta G_{\text{global}}^0 < 0$) the acid–base equilibria have to compensate for this loss in resonance energy ($K_{\text{a(B-H)}}^{-1} K_{\text{a(H-L)}} > 1$ such that $K_{\text{global}} > 1$). In other words, when we rationally analyse this reaction, it seems that the acid base reactions deliver the driving force necessary for the q.m. formation. More specific, both $K_{\text{a(B-H)}}^{-1}$ and $K_{\text{a(H-L)}}$ have to be as large as possible or, in other words, the p*K*_a difference between the base (B⁻) added and the acid H–L, in the polymerisation solvent used, is proportional with the strength of the driving force. This means that the p*K*_s[33] of the polymerisation solvent plays a determining role in the

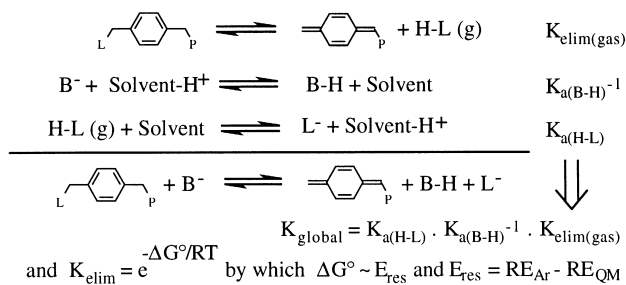


Fig. 2. Global reaction of the q.m. formation splitted into the basic reactions.

Table 4
Comparison of the polymerisation results of **5a–d**

Solvent	pK _s [40]	5d		5c		5a	
		$\bar{M}_w (\times 10^4)$	Yield (%)	$\bar{M}_w (\times 10^4)$	Yield (%)	$\bar{M}_w (\times 10^4)$	Yield (%)
MMF	11	80.3	25	20.5	5	0.0	0
<i>s</i> -Butanol	22–26 ^a	23.8	90	17.8	15	0.0	0
CH ₂ Cl ₂	— ^b	35.0	75	36.8	55	7.3	10
NMP	24	30.0	35	16.5	30	5.6	35
DMSO	33	45.4	80	24.5	45	4.9	45

^a As pK_s(butanol) = 22 and pK_s(*t*-butanol) = 26, we expect that pK_s(*s*-butanol) is situated between these two values.

^b Not found in the literature.

q.m. and thus the polymer formation as it sets a limit on the strength of the base B[−] and the acid H–L in the solvent considered.

To verify the model proposed, the synthesised monomers are polymerised in several solvents with different pK_s values (see Tables 1, 3 and 4). In this way we vary the strength of the base and acid and hence, at least according to our postulated model, the driving force.

The monomers are synthesised via a common procedure. In the first step the methyl esters are reduced to their corresponding alcohol with LiAlH₄ in dry THF [31]. Next, these alcohols are chlorinated by means of HCl and ZnCl₂ [32]. The thioethers **4a–e** are synthesised with *n*-alkylthiol, NaOH and a phase transfer reagent, Aliquot 336, in water and toluene [34]. These sulphides are used without any purification for the oxidation to the sulphoxide **5a–e** with H₂O₂ and TeO₂ in methanol or dioxane [35] (see Fig. 3).

The polymerisation of monomer **5a** was investigated in seven solvents or solvent mixtures. In every experiment Na⁺*t*BuO[−] was used as the base. When the reaction was carried out in a solvent with a low pK_s, like *N*-methylformamide (MMF), or a mixture of MMF and CH₂Cl₂ (CH₂Cl₂ was added because of the low solubility of **5a** in MMF) no polymer was found. Also in other protic but less polar solvents, like *s*-butanol or *t*-butanol, the polymerisation was not successful. Subsequently we switched to aprotic solvents with a high pK_s, like DMSO or *N*-methylpyrrolidone

(NMP). To the DMSO some THF was added to improve the solubility of monomer **5a**. In this mixture a polymer with a bimodal molecular weight distribution (m.w.d.) was formed. It was possible to separate the high molecular weight polymer fraction from the monomers and the low molecular weight fraction by means of a precipitation in a mixture of ether and THF (7/3). It is also possible to polymerise the biphenyl derivative **5a** in NMP. The m.w.d. of the polymer formed in this solvent also has a bimodal character. Again it is possible to separate the low and high molecular weight. From each polymer fraction the yield was determined and from each polymer the molecular weight (\bar{M}_w) and polydispersity ($\bar{M}_w/\bar{M}_n = D$) are established by means of size exclusion chromatography (s.e.c.) measurements (eluent: DMF).

A question now arising, is whether the polymerisation of **5a–b** performed in aprotic solvents is indeed a radical chain polymerisation and proceeds via the biphenyl-*p*-quinodimethane intermediate, or is an anionic polymerisation by which a benzylic anion attacks a benzylic chloride (Fig. 4). This question can be answered by means of u.v.–vis. absorbance measurements accomplished during the course of the polymerisation as the benzoid and quinoid structures of **5b** absorb at different wavelengths. During the u.v.–vis. measurements we clearly detected an absorption at 445 nm that increased very fast and then disappeared fast but gradually. Most probably this signal descends from the

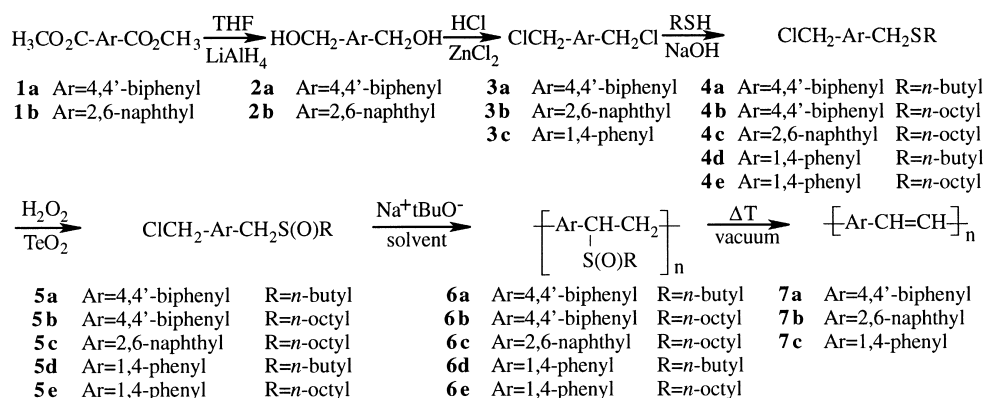


Fig. 3. Synthesis of the conjugated polymers **7a–c**.

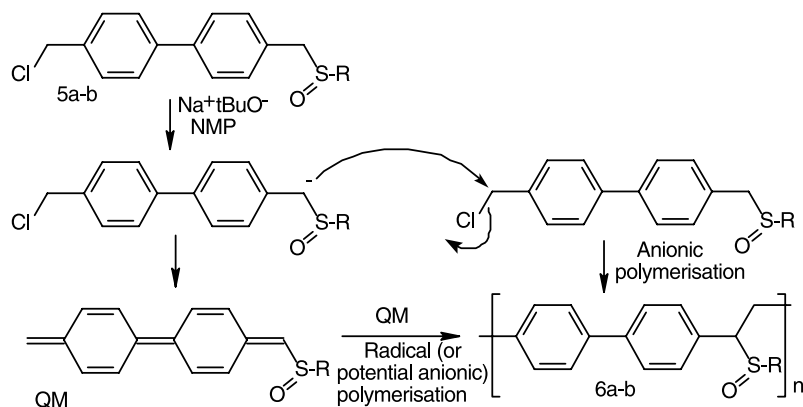


Fig. 4. Both the anionic and radical mechanism.

biphenyl-*p*-quinodimethane system in view of literature data [36–38]. Whereas during the polymerisation the concentration of the *p*-quinodimethane decreases, the concentration of the benzoid structure **5b** increases, which is expressed in an isosbestic point like indicated in Fig. 5. As we establish a build-up of the biphenyl-*p*-quinodimethane concentration, which is consumed afterwards, this polymerisation can proceed via a radical chain mechanism as substantiated in earlier work [24].

This assumption was confirmed by the experiments performed to shed some light on the bimodal m.w.d.. Indeed, the following experiments prove that the bimodal m.w.d. is caused by the simultaneous appearance of two polymerisation mechanisms. If 0.5 equivalents of the radical inhibitor 2,2,6,6-tetramethyl-1-piperidiniloxy (TEMPO) is added to the polymerisation of **5b** in NMP, only the low molecular weight is obtained, whereas if 5% water (with respect to the NMP) is added, only the high molecular weight part is formed (Fig. 6). Consequently, TEMPO inhibits the radical polymerisation of the biphenyl-*p*-quinodimethane system, while water inhibits the anionic

polymerisation of **5b** and/or the biphenyl-*p*-quinodimethane system [39].

Another aprotic but more apolar solvent, in which the polymerisation is possible, is CH_2Cl_2 . The polymer synthesised in this solvent exhibits a monomodal weight distribution. As we expected, the polymerisation carried out in this “apolar” solvent proceeds exclusively according to a radical mechanism. This is confirmed by the addition of TEMPO to the polymerisation of the biphenyl monomer **5b** as only a low amount of low molecular weight material is formed.

The naphthyl derivative **5c** was polymerised in the solvents summarised in Table 3. In some cases a co-solvent was added in order to improve the solubility of **5c**. In two cases (DMSO/THF, THF), we added less than 1.3 equivalents of the base Na^+tBuO^- , as we noticed that using 1.3 equivalents of this base causes partial elimination in NMP and CH_2Cl_2 . The polymer was precipitated in a mixture of ether and THF (7/3), in order to separate the high molecular weight polymer from the low molecular weight material and the monomer. We noticed also in this case that the m.w.d. of the polymers, synthesised in aprotic polar solvents, are bimodal, whereas the m.w.d. of the polymers synthesised in other solvents are monomodal. In all solvents high molecular weight polymers are obtained. This result contrasts with the polymerisation of **5a–b**, as these monomers only polymerise in aprotic solvents. In fact as expected, this is a consequence of the lower resonance energy of **5c** which is lost when the 2,6-naphthalene-*p*-quinodimethane intermediate is formed.

When the polymerisation results of the phenyl (**5d**) [24–26], naphthyl (**5c**) and biphenyl (**5a**) derivatives, obtained in the same solvent are compared (Table 4), we perceive that lower molecular weights and yields are gained if a monomer with a larger resonance energy is used. In other words, for a polymerisation carried out in the same solvent counts that $\bar{M}_w 5d > \bar{M}_w 5c > \bar{M}_w 5a$ and $\text{yield } 5d > \text{yield } 5c > \text{yield } 5a$. As appears from these results it seems that the polymerisation of a monomer with a higher resonance

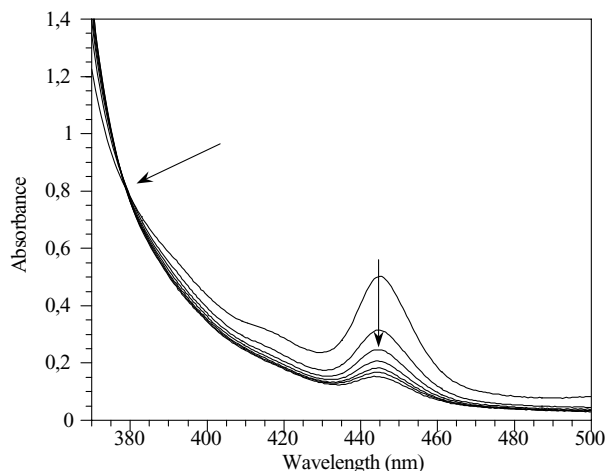


Fig. 5. U.v.-vis. measurement in NMP.

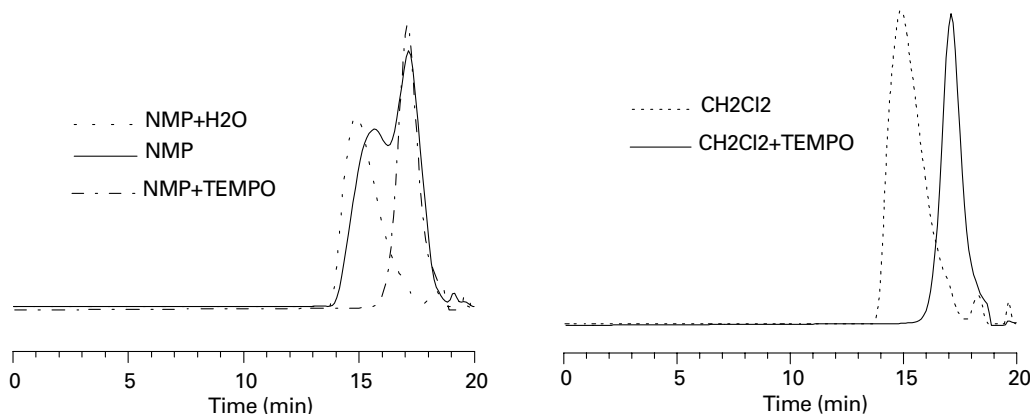


Fig. 6. Polymerisation of **5b** in NMP + H₂O or TEMPO (left) or CH₂Cl₂ + TEMPO (right).

energy requires a solvent with a higher pK_s [40], although the solvation of the benzylic anion also plays an important role. Indeed, protic solvents stabilise this anion while aprotic solvents do not. Nevertheless, this is beyond the scope of this work and will be discussed in a future work [41]. Applied to the polymerisation of the 2,6-naphthyl derivative **5c** this means that the yield of polymerisation is proportional with the pK_s of the solvent used. Thus, $pK_s(\text{MMF}) < pK_s(s\text{-butanol}) < pK_s(\text{aprotic solvents})$ and $\text{yield}(\text{MMF}) < \text{yield}(s\text{-butanol}) < \text{yield}(\text{aprotic solvents})$. As mentioned before, this applies even to a greater extent for the 4,4'-biphenyl derivatives **5a–b** as the resonance energy of these derivatives is higher. In protic solvents like MMF or *s*-butanol the polymerisation of monomer **5a** even does not go on.

Like already reasoned in the beginning of this paper, it appears from these results that the driving force necessary for the formation of the quinoid system is proportional with the strength of the base used in the polymerisation. Thus, a stronger base gives rise to a stronger driving force when the same leaving group is used. In this sense, the basicity of the solvent used is important as a rather acid solvent will level down a stronger base.

3.2. Conversion to the conjugated polymers

To shed some light on the properties of the corresponding conjugated polymers, the soluble precursors are converted to their conjugated not soluble form by means of a thermal treatment. The conversion is carried out under vacuum, in order to avoid the oxidation of the vinylenes bonds [42] and to improve the evaporation of the elimination products. During this treatment the sulphoxides are eliminated and double bonds are formed. The elimination of these sulphoxides proceeds via a cyclic mechanism and delivers mainly *trans* structures [43]. In this case the eliminated sulphenic acids are not stable and react further to water, thiosulphonates and disulphides.

The thermal elimination of the sulphoxide groups and the degradation of the conjugated polymers are, among others, examined with thermal gravimetric analysis (t.g.a.). The precursor polymers **6a** and **6c** exhibit a first region of weight loss between 120 and 310°C. The weight loss approaches the theoretical amount of the elimination of the sulphenic acid. A second weight loss is observed for both polymers around 530°C and corresponds with the degradation of the conjugated polymer (see Fig. 7, left).

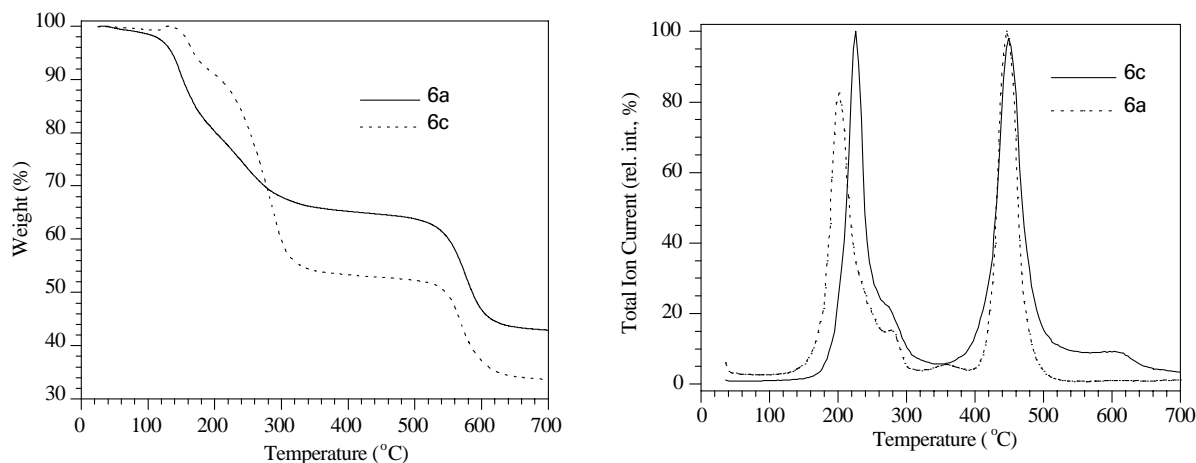


Fig. 7. T.g.a. (left) and d.i.p.-e.i. (right) of **6a** and **6c**.

Table 5
Positive fragment ions of elimination products

Positive fragment ions(<i>n</i> -butyl)	<i>m/z</i>	Positive fragment ions (<i>n</i> -octyl)	<i>m/z</i>
<i>n</i> -Butyl-S–S(O)- <i>n</i> -butyl	194	<i>n</i> -Octyl-S–S(O)- <i>n</i> -octyl	306
<i>n</i> -Butyl-S–S- <i>n</i> -butyl	178	<i>n</i> -Octyl-S–S- <i>n</i> -octyl	290
<i>n</i> -Butyl-SOH	106	<i>n</i> -Octyl-S(O)OH	178
<i>n</i> -butyl-S	89	<i>n</i> -Octyl-S(O)	161
<i>n</i> -Butyl	57	<i>n</i> -Octyl-S	145
		<i>n</i> -Pentyl	71
		<i>n</i> -Butyl	57
		<i>n</i> -Propyl	43

Further the conversion of the precursor polymers **6a** and **6c** to their conjugated form and the degradation of the conjugated polymers **7a–b** is analysed by means of d.i.p.–m.s. (e.i.) measurements (direct insert probe-electron impact) (Fig. 7). The total ion current curves versus temperature of polymers **6a** and **6c** show two separate signals. The first signal is caused by the fragment ions of the elimination products (Table 5), the second signal corresponds with the degradation of the conjugated polymer. Thermal gravimetric data already showed that a high amount of char residue remains after the degradation. This residue consists of cross-linked polymers and condensed aromatic units which possess a high thermal stability [44–45].

The conversion of the precursors to their conjugated form is also monitored by means of f.t.-i.r. spectroscopy. For this a solution of the polymer in CHCl₃ is applied on a KBr substrate, dried and treated under vacuum at a certain temperature. At different points of time the treatment is interrupted and i.r. measurements are carried out. Both the polymers **6a** and **6c** are heated at 140, 180, 220 and 240°C. Measurements are performed before the heat treatment and after 10, 30, 60, 120, 180 and 240 min. In Fig. 8 the course of the i.r. signals in function of the time during the conversion of **6a** to **7a** at 180°C is shown. The signals appearing at 3012 and 959 cm⁻¹ are caused by the double bonds which arise during the conversion while the sulphoxide signal at

1030 cm⁻¹ completely disappears. However, even after 240 min of treatment small signals at 2870, 2928 and 2958 cm⁻¹, most probably caused by the elimination products, remain. This explains the difference between the theoretical and experimental weight observed after elimination with t.g.a. measurements. When the conversion of **6c** to **7c** is followed with i.r. measurements, the same tendency of the i.r. signals is observed. According to these measurements the optimal time and temperature for the conversion are 30 min at 220°C for both **6a** and **6c** at given pressures (see Section 2).

Solutions of the precursor polymers **6a** and **6c** were applied to a quartz substrate and subjected in vacuo to 200°C during 1.5 h and 220°C during 2 h, respectively. The u.v.–vis. spectra of these films are shown in Fig. 9. The absorption maximum of the greenish polymer **7a** (386 nm) is blue shifted relative to PPV (424 nm). The maximum of the absorption band of **7b** (426 nm) and PPV (**7c**, obtained from **6d**) are almost the same. The edge of the absorption band of the naphthyl and biphenyl derivative are situated near 2.51 and 2.68 eV, respectively (**7c**: 2.35 eV). The band gap and the maximum of the absorption band of PPV synthesised according to the Wessling precursor route are almost equal to the results of **7c** [46].

The photoluminescence measurements were carried out on the same samples as used for the u.v.–vis. measurements and are illustrated in Fig. 9. PPV (**7c**) synthesised according

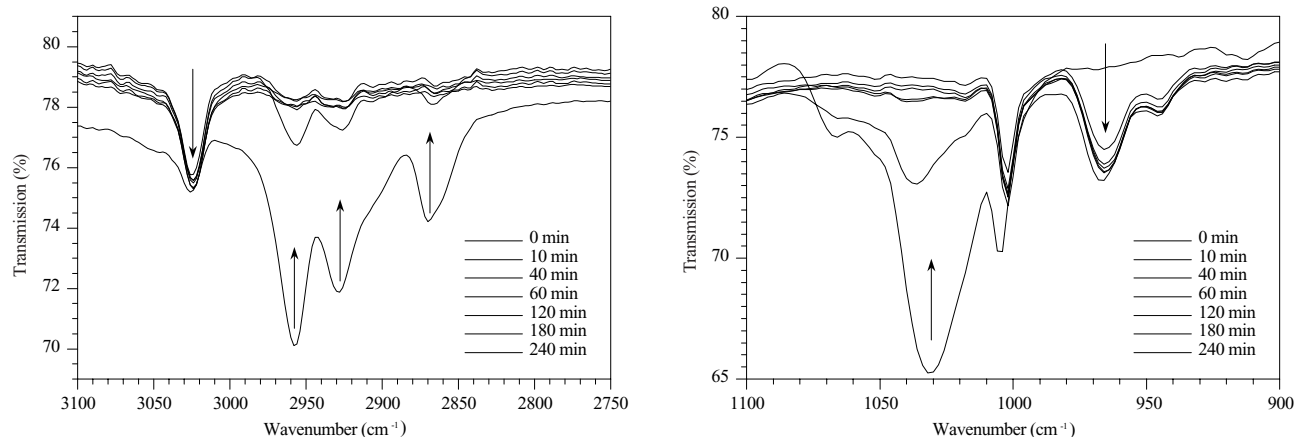


Fig. 8. Decrease of alkyl signals and increase of vinyl signal (left) and decrease of sulphoxide signal and appearance of vinyl signal (right).

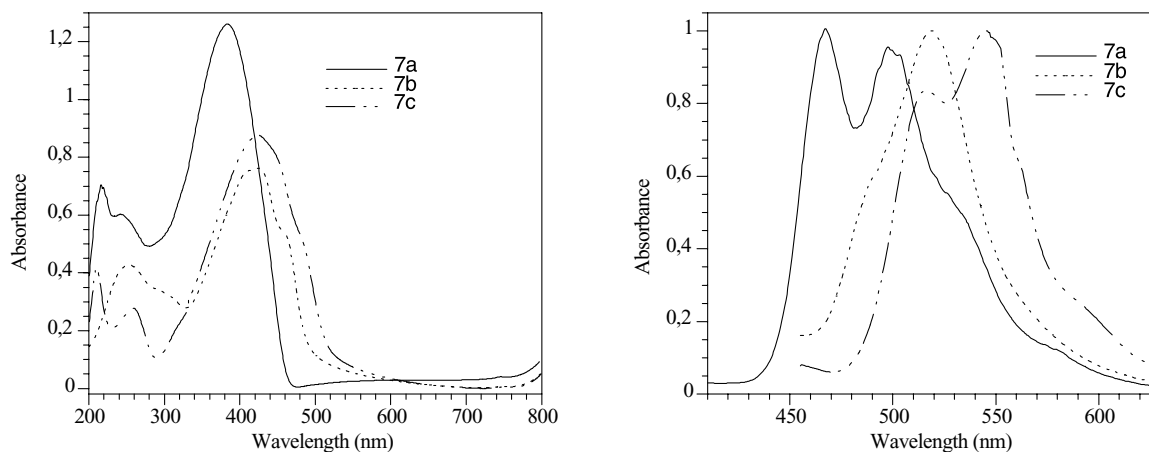


Fig. 9. U.v.-vis. (left) and photoluminescence (right) spectra of **7a–c**.

to our route emits yellow light with a maximum at 544 nm and a shoulder at 516 nm. The PPV obtained via the Wessling route shows a similar photoluminescence spectrum. A film eliminated onto glass at 170°C ($p = 10^{-3}$ mbar, $t = 2$ h) shows a maximum at about 542 nm with a shoulder at 518 nm. Hereby it is of importance to note that the elimination circumstances play an important role in the shape and position of the photoluminescence spectra[47]. The spectrum of polymer **7b** is blue shifted compared to PPV, has a maximum at 518 nm and emits greenish light. The biphenyl derivative **7a** shows emission maxima at 467 and 497 nm which corresponds with the green–blue light.

4. Conclusions

Chain polymerisations used for the synthesis of poly(arylene vinylene)s proceed via a quinoid compound. The formation of this quinodimethane system is coupled with the loss of resonance energy of the aromatic monomer. This loss of energy must be compensated by a driving force. In order to comprehend this driving force, monomers with an increasing resonance energy, the 1,4-phenyl, 2,6-naphthyl and 4,4'-biphenyl derivatives, are polymerised via the sulphanyl precursor route. Like expected, the best results, this means the highest yields and molecular weights, are obtained when aprotic solvents are used. Despite the high resonance energy of **5a**, u.v.-vis. measurements prove that in these solvents the driving force, which is the pK_a difference between the base added and the acid derived from the leaving group after the 1,6-elimination, is strong enough to deliver the energy necessary for the q.m. formation. After the polymerisation bimodal molecular weight distributions are obtained. Addition of water and TEMPO revealed the cause of this bimodal molecular weight character. It seems that in polar aprotic solvents two kinds of polymerisation mechanisms can occur at the same time, a radical chain polymerisation generating higher molecular weights, and

an anionic polymerisation, delivering lower molecular weights. The conversion of both polymers **6a** and **6c** to their corresponding conjugated polymer is followed with t.g.a., d.i.p.-e.i. and f.t.-i.r. measurements. As expected, the photoluminescence of the conjugated polymers **7a–b** shifts to the blue relative to PPV.

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