ELSEVIER

Polymer 41 (2000) 7003–7009

polymer

Synthesis of electron-rich versus electron-poor poly{[1,4-phenylene]-[1-(*n*-alkylsulfinyl)ethylene]}s via the sulfinyl precursor route in different organic solvents

P. Adriaensens, M. Van Der Borght, L. Hontis, A. Issaris, A. van Breemen, M. de Kok, D. Vanderzande*, J. Gelan

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

Received 20 July 1999; received in revised form 17 December 1999; accepted 19 January 2000

Abstract

In this paper new insights in the mechanism of the sulfinyl precursor route towards poly(phenylene vinylene) (PPV) derivatives are presented by studying the polymerisation reaction in various solvents and by evaluating the influence of both electron donating and withdrawing substituents. A strong indication is presented that in alcohols the expulsion of the leaving group is involved in the rate determing step of the reaction, the formation of the *p*-quinodimethane intermediate, which further also depends on the type of solvent and substituents. Moreover, two polymerisation mechanisms can occur simultaneously: a radical mechanism that results in high molecular weight polymers and an anionic mechanism yielding low molecular weights. Competition between both mechanisms strongly depends on the solvent and type of substituents. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(phenylene vinylene)s; Synthesis; Polymerisation mechanism

1. Introduction

Polymer-based light emitting diodes (PLEDs) in which thin films of conjugated polymers constitute the active layer were first reported in 1990 by Friend et al. [1]. Interest in this field then grew rapidly and extensive research was performed in order to improve the active materials and the performance of devices [2,3]. Nowadays the electroluminescence and lifetime of PLEDs is sufficient to compete with classical inorganic LEDs.

Precursor routes are of major importance towards the development of optical and electronic applications of organic semiconductors since they introduce processability which makes the incorporation of these materials into devices feasible. Several routes have been developed of which the Gilch [4], the Wessling [5], the xanthate [6,7] and the sulfinyl [8–10] routes are the most important. A general scheme of the precursor routes towards the formation of poly(phenylene vinylene) (PPV) and derivatives is presented in Fig. 1. The first step is a proton abstraction of the *p*-xylene derivative (pre-monomer) **1** followed by a 1,6-elimination with expulsion of the leaving group (L). In this way the actual monomer, a *p*-quinodimethane system **2** is generated. Once this *p*-xylylene intermediate is formed, it polymerises spontaneously and rapidly (without external initiation) to yield high molecular weight PPV precursor polymers **3** (step 2). The conjugated structure **4** can be obtained by thermal treatment.

The sulfinyl route developed in our laboratory differs from the other precursor routes in that a chemical differentiation is introduced between the leaving group, a halide, and a so-called polariser, a sulfinyl group ($S(O)R_3$). This results in unsymmetrical monomers. The sulfinyl group has several functions: besides the preferential stabilisation of the anion formed in the first step of the process and the polarisation of the *p*-quinodimethane system in such a way that regular head-to-tail addition results, it offers control over the stability of the precursor polymer. Also the solubility of both the monomer and precursor polymer can be altered by changing the R_3 group of the non-ionic polariser. This not only means that the physico-chemical characterisation of the precursor polymer becomes more straightforward but also that a broad range of solvents becomes available for processing, e.g. alcohols, which can be interesting from an environmental point of view. Moreover the polymerisation

* Corresponding author. Tel.: + 32-11-268-321; fax: + 32-11-268-301.
E-mail address: dirk.vanderzande@luc.ac.be (D. Vanderzande).

0032-3861/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00071-9

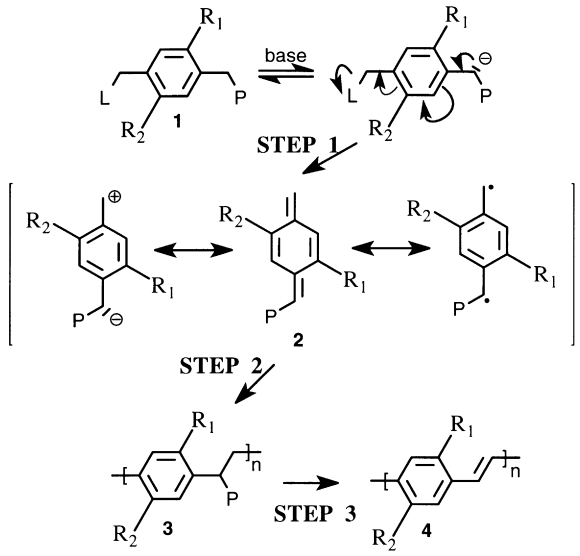


Fig. 1. General scheme of the polymerisation reaction.

itself can be investigated in various solvents and tuned more efficiently.

The polymerisation reaction however is a complicated process in which the different steps are highly linked and the influence of the solvent and aromatic ring substituents (R_1 and R_2) is rather unknown. Also the mechanism of these *p*-quinodimethane based polymerisations is unclear: both anionic [11–13] and radical [5,14,15] mechanisms have been proposed.

In this paper new insights in the mechanism are presented by studying this type of polymerisation in various solvents and by evaluating the influence of both electron donor and acceptor substituents (R_1 and R_2). Especially the introduction of electron acceptors is of interest towards the use of PPV derivatives as active layers in PLEDs. Although the electroluminescence efficiency is high in PLEDs with calcium as cathode, the lifetime is rather limited due to the reactivity of calcium [16,17]. However, since the work function of aluminum, a less reactive metal, is higher as compared to calcium, a higher electron affinity of the conjugated polymer is required in order to retain the high PLED efficiencies.

Table 1
Overview of monomers and precursor polymers

Pre(monomer)				Precursor polymer		
	L	$R_{1,2}$	R_3		$R_{1,2}$	R_3
1a	Cl	H	*n*-Butyl	**3a**	H	*n*-Butyl
1a′	I	H	*n*-Butyl	**3a**	H	*n*-Butyl
1b	Cl	H	*n*-Octyl	**3b**	H	*n*-Octyl
1c	Cl	CH_3	*n*-Butyl	**3c**	CH_3	*n*-Butyl
1d	Cl	CH_3	*n*-Octyl	**3d**	CH_3	*n*-Octyl
1e	Cl	OCH_3	*n*-Butyl	**3e**	OCH_3	*n*-Butyl
1f	Br	Cl	*n*-Octyl	**3f**	Cl	*n*-Octyl
1g	H	H	*n*-Octyl	–	–	–

2. Experimental

2.1. Materials

All solvents and reagents are purchased from ACROS or Aldrich and are used without further purification. The syntheses of the starting unsymmetrically substituted monomers **1a–f** (Table 1) is described elsewhere [18–20]. The synthesis of the blocked monomer **1g** (L = H; see Table 1) follows the general procedure described in Ref. [17] (phase transfer catalysed substitution reaction).

2.2. Analyses

^{13}C and ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 Spectrometer at 100 and 400 MHz, respectively. Chemical shifts are expressed in ppm relative to TMS. Fourier transform infrared (FT-IR) spectroscopy was performed on a Perkin–Elmer 1600 FT-IR. Molecular weights were determined relative to polystyrene standards (Polymer Labs) by size exclusion chromatography (SEC) on a Spectra series P100 (Spectra Physics) equipped with two MIXED-B columns (10μm, 2 cm × 30 cm, Polymer Labs) and a RI detector (Shodex) at 70°C with a flow rate of 1.0 ml/min. Glass transition temperatures (T_g) were determined by modulated differential scanning calorimetry (TA Instruments 2000) in closed Al pans (heating rate of 2.5°C/min, amplitude of 1.5°C, period of 60 s, temperature calibration with In and benzophenone, C_p calibration with a PMMA NIST standard).

2.3. Standard procedure for the polymerisation

A solution of monomer (1 mmol) in solvent (7 ml) and a solution of NaO*t*Bu (base) in solvent (3 ml) were flushed with N_2 under stirring for 1 h before mixing. After 1 h reaction under a constant stream of N_2 the reaction mixture was poured in 100 ml H_2O, neutralised with 1.0 M HCl and extracted twice with 100 ml $CHCl_3$. The combined organic layers were concentrated under reduced pressure, dissolved in 10 ml $CHCl_3$ and precipitated in 100 ml of an appropriate solvent. The polymer was collected, filtered and dried under vacuo. For polymerisations in CH_2Cl_2 the base was introduced in its solid phase. The standard amount of 1.3 equiv of NaO*t*Bu was sometimes slightly reduced to prevent basic elimination of sulfinyl groups. The type of reaction solvent, precipitation solvent, amount of base and reaction temperature is given below for each of the precursor polymers. The polymer yields, molecular weights and molecular weight distributions are given in Table 2.

Table 2
Overview of the polymer yield, molecular weight and molecular weight distribution of different precursor polymers obtained via the Sulfinyl precursor route in various solvents

Entry	L[a]	R_3[b]	$R_1 = R_2$[c]	Solvent	Yield (%)	$\bar{M}_w$ ($\times 10^{-4}$) (g/mol)	$\bar{M}_w/\bar{M}_n$[d]
1	Cl	*n*-Butyl	OMe	MeOH	40	8.8	1.7(m)
2	Cl	*n*-Butyl	H	MeOH	0	–	
3	Br	*n*-Octyl	Cl	MeOH	0	–	
4	I	*n*-Butyl	H	MeOH	25	7.4	1.7(m)
5	Cl	*n*-Butyl	Me	MMF	25	62.0	2.9(m)
6	Cl	*n*-Butyl	OMe	MMF	35	26.7	1.8(m)
7	Cl	*n*-Butyl	H	MMF	25	80.3	2.7(m)
8	Br	*n*-Octyl	Cl	MMF	0	–	
9	Cl	*n*-Butyl	Me	*s*-BuOH	90	77.3	2.6(m)
10	Cl	*n*-Octyl	H	*s*-BuOH	88	23.8	2.0(m)
11	Cl	*n*-Butyl	H	*s*-BuOH	87	54.0	2.5(m)
12	Br	*n*-Octyl	Cl	*s*-BuOH	65	67.8	3.3(m)
13	Cl	*n*-Octyl	Me	THF	65	98.9	3.4(m)
14	Cl	*n*-Octyl	H	THF	80	73.5	3.9(b)
15	Br	*n*-Octyl	Cl	THF	50	12.1	6.2(b)
16	Cl	*n*-Butyl	Me	NMP	55	19.2	1.9(m)
17	Cl	*n*-Butyl	H	NMP	45	2.5	5.3(b)
18	Br	*n*-Octyl	Cl	NMP	35	2.6	3.4(b)
19	Cl	*n*-Butyl	H	MMF[e]	0	–	
20	Cl	*n*-Butyl	H	NMP[e]	20	0.3	1.1(m)
21	Cl	*n*-Butyl	H	NMP(H_2O	50	6.1	1.7(m)
22	Br	*n*-Octyl	Cl	CH_2Cl_2	70	31.3	4.5(m)

[a] L is the leaving group.
[b] R_3 is the *n*-alkyl group of the polariser.
[c] R_1 and R_2 are the aromatic ring substituents.
[d] (m) and (b) denote monomodal and bimodal molecular weight distribution, respectively.
[e] With 0.5 equiv of TEMPO.

2.4. Poly{[1,4-phenylene]-[1-(n-butylsulfinyl)ethylene]} **3a**

This compound was synthesised according to the general procedure starting from **1a** or **1a′**. With chlorine as leaving group (**1a**): reaction in MeOH: 20°C, 1.3 equiv base; in MMF: 20°C, 1 equiv base; in *s*-BuOH: 30°C, 1.3 equiv base; in NMP: 20°C, 1.1 equiv base and in DMSO: 20°C, 1 equiv base. With iodine as leaving group (**1a′**): reaction in MeOH: 20°C, 1.3 equiv base. The polymers were precipitated in ether. The analysis of these compounds is described elsewhere [8,19]. NMP was used as the eluent for SEC except for the polymers obtained in NMP for which DMF was used.

2.5. Poly{[1,4-phenylene]-[1-(n-octylsulfinyl)ethylene]} **3b**

This compound was synthesised according to the general procedure starting from **1b**. Reaction in *s*-BuOH: 30°C, 1.3 equiv base and in THF: 30°C, 1 equiv base. The polymers were precipitated in a mixture of ether and hexane (1/1). The analysis of these compounds is described elsewhere [21]. DMF was used as the eluent for SEC except for the polymers obtained in MeOH for which NMP was used.

2.6. Poly{[2,5-dimethyl-1,4-phenylene]-[1-(n-butylsulfinyl)ethylene]} **3c**

This compound was synthesised according to the general procedure starting from **1c**. Reaction in *s*-BuOH: 20°C, 1.3 equiv base; in MMF: 20°C, 1.3 equiv base; in NMP: −10°C, 1.3 equiv base and in DMSO: 20°C, 1.3 equiv base. All polymers were precipitated in ether. DMF was used as the eluent for SEC. $T_g = 77$°C; IR (KBr, ν, cm^{-1}): 2959, 2931, 2871, 1505, 1457, 1181, 1035; ^{1}H NMR (( ) = integration value): 7.32, 6.85, 6.51 (2H), 3.89 (1H), 3.73, 3.45, 3.09, 2.91 (2H), 2.26, 2.14, 2.03, 1.97 (8H), 1.63, 1.53 (2H), 1.30, 1.23 (2H), 0.82, 0.80 (3H); ^{13}C NMR: 136.56, 136.06, 134.76, 133.84, 133.51, 131.88, 131.12, 132.41, 129.05, 65.76, 65.05, 59.50, 49.11, 48.36, 34.11, 25.07, 24.78, 22.03, 21.79, 19.13, 18.91, 13.55.

2.7. Poly{[2,5-dimethyl-1,4–phenylene]-[1-(n-octylsulfinyl)ethylene]} **3d**

This compound was synthesised according to the general procedure starting from **1d**. Reaction in THF: 20°C, 1 equiv base. The polymer was precipitated in a mixture of ether and hexane (1/1). DMF was used as the eluent for SEC. $T_g =$ 63°C; IR (KBr, ν, cm^{-1}): 2987, 2958, 2889, 1525, 1467, 1058; ^{1}H NMR (( ) = integration value): 6.85, 6.57 (2H), 3.92, 3.65, 3.45, 2.97 (3H), 2.32, 2.14, 1.89, 1.63 (10H), 1.18 (10H), 0.82 (3H); ^{13}C NMR: 136.95, 136.58, 135.32, 134.21, 132.91, 132.18, 129.46, 65.77, 49.58, 34.59, 32.00, 29.42, 29.30, 28.99, 23.34, 22.89, 19.34, 14.41.

2.8. Poly{[2,5-dimethoxy-1,4-phenylene]-[1-(n-butylsulfinyl) ethylene]} **3e**

This compound was synthesised according to the general procedure starting from **1e**. Reaction in MeOH: 35°C, 1.3 equiv base and in MMF: 20°C, 1.3 equiv base. The polymers were precipitated in ether. DMF was used as the eluent for SEC. $T_g = 67$°C; IR (KBr, ν, cm^{-1}): 2940, 2910, 2850, 1495, 1450, 1385, 1215, 1025; ^{1}H NMR (( ) = integration value): 6.95, 6.86, 6.56, 6.39, 6.32 (2H), 4.45 (1H), 3.80, 3.70, 3.56, 3.51, 3.46, 3.41, 3.37, 3.32 (6H), 3.24 (2H), 1.91, 2.15, 2.45 (2H), 1.46, 1.66 (2H), 1.32, 1.24 (2H), 0.82 (3H); ^{13}C NMR: 151.61, 150.81, 127.35, 126.87, 122.37, 121.32, 114.80, 114.20, 113.53, 111.55, 110.71, 59.30, 54.70, 56.14, 55.73, 49.45, 48.67, 31.84, 29.35, 28.74, 24.90, 24.51, 22.08, 21.87, 13.59.

2.9. Poly{[2,5-dichloro-1,4-phenylene]-[1-(n-octylsulfinyl) ethylene]} **3f**

This compound was synthesised according to the general procedure starting from **1f**. Reaction in MMF: 20°C, 1.1 equiv base; in THF: 20°C, 1 equiv base; in NMP: 20°C, 1 equiv base; in DMSO: 20°C, 1 equiv base; in MeOH: 20°C, 1.3 equiv base; in CH_2Cl_2: 20°C, 1.2 equiv base and in *s*-BuOH: 20°C, 1 equiv base. The polymers were precipitated in a mixture of ether and hexane (1/1). THF was used as the eluent for SEC. $T_g = 75$°C; IR (KBr, ν, cm^{-1}): 2954, 2925, 2854, 1479, 1372, 1080, 1052; ^{1}H NMR (( ) = integration value): 7.64, 7.20, 7.01 (2H), 4.47 (1H), 3.71, 3.48, 3.21 (2H), 2.49, 2.35 (2H), 1.68 (2H), 1.20 (10H), 0.81 (3H); ^{13}C NMR: 136.43, 133.46, 132.28, 130.75, 130.35, 56.87, 61.52, 49.95, 33.49, 35.05, 31.59, 28.66, 28.88, 29.05, 22.50, 23.06, 14.01.

2.10. UV–Vis spectroscopy

To achieve efficient mixing of the reagents, a magnetic stirrer was added to the solution of monomer (2 ml) in the quartz cell of the spectrometer. While the monomer solution is stirring, the solution of NaO*t*Bu (1 ml) is added. Spectra were acquired from 240 to 440 nm at programmed time intervals, or the change in λ_{max} was monitored in time. The scan rate was 520 nm/min and the scan interval 0.5 nm. To solutions in THF one drop of water was added, in order to keep the reaction mixture clear during the measurement.

3. Results and discussion

Table 2 shows an overview of the polymer yield, molecular weight and molecular weight distribution of different precursor polymers obtained via the sulfinyl precursor route in several solvents by varying the leaving group, polariser and substituent R_{1-2}. With chlorine as leaving group the polymerisation of pre-monomers in methanol only takes place if electron donor substituents are present (entries 1–3). In MMF, another protic, polar solvent, polymerisation occurs except in the presence of electron acceptors (entries 5–8). In both solvents a rather low yield and a monomodal molecular weight distribution is obtained.

In protic, more apolar solvents like *s*-butanol, polymerisation always takes place with a high yield and a monomodal molecular weight distribution (entries 9–12). Electron acceptors however also seem to reduce the polymer yield.

In aprotic, apolar solvents like THF polymerisation also occurs (entries 13–15) but a monomodal molecular weight distribution is only observed in the presence of electron donor substituents. Using unsubstituted or electron acceptor substituted pre-monomers results in a bimodal molecular weight distribution which strongly complicates the comparison of polymer yields.

In aprotic, more polar solvents like NMP and DMSO (results not shown) similar trends are observed. A monomodal molecular weight distribution is only observed if electron donor substituents are used (entries 16–18).

Since the polymerisation of sulfinyl monomers proceeds via a *p*-xylylene intermediate **2**, an efficient conversion of pre-monomer **1** to the actual monomer, the *p*-quinodimethane system **2**, is essential for a high polymer yield. UV–Vis spectroscopy has proven to be the most convenient technique to monitor the concentration of polymerising unsubstituted *p*-xylylenes [14]. Differentiation is based on the difference in absorption wavelength for a benzoic (278 nm) and a quinoid (316 nm) structure [8,13,22,23]. This difference in λ_{max} is further confirmed in this paper by observing a reaction as for entry 7 but in which the blocked pre-monomer **1g** (Table 1), has chlorine as the leaving group replaced by hydrogen, is used. No absorption is observed at 316 nm since only the benzylic anion but not the quinodimethane system can be formed. Applying this technique for monitoring the appearance and depletion of the *p*-xylylene intermediate for unsubstituted monomers results in a plot as depicted in Fig. 2 for entry 7. Similar plots are obtained for the polymerisation in *s*-butanol [21], in which high concentrations of the *p*-quinodimethane intermediate are easily formed, and for unsubstituted 4,4′-biphenylene type monomers in NMP [24]. Fig. 3 shows the appearance and depletion of the *p*-xylylene intermediate in THF for entry 15. It indicates that also in the presence of electron acceptor substituents the polymerisation proceeds via the *p*-quinodimethane system.

The polymerisation reaction is a complex process in which several, highly linked steps can be distinguished. Although it is beyond the scope of this paper to explain the complete mechanism, some interesting points can be deduced. The absence of polymerisation of unsubstituted and electron acceptor substituted pre-monomers in methanol (entries 2 and 3) and electron acceptor substituted pre-monomers in MMF (entry 8) can be ascribed to the inability of quinoid formation as was already demonstrated

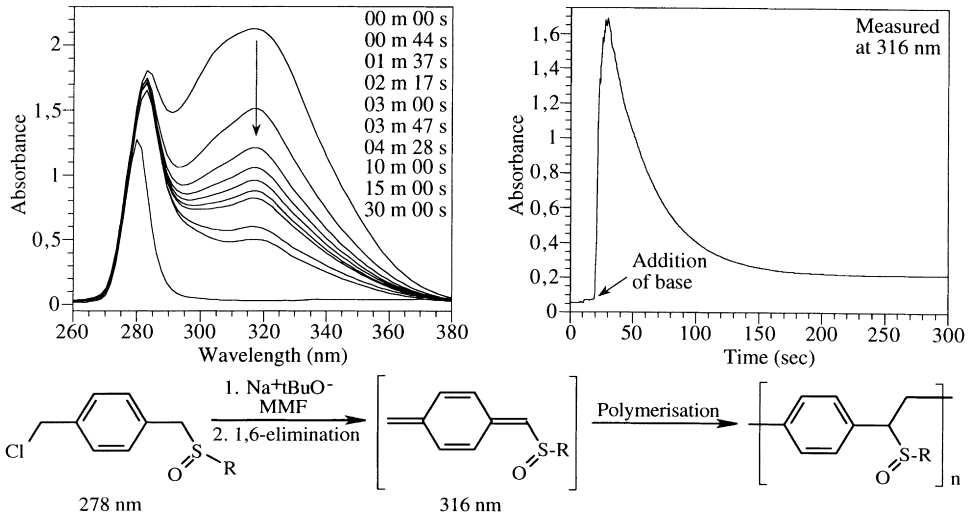


Fig. 2. UV–Vis visualisation of the formation and consumption of the *p*-quinodimethane intermediate for **1a** in MMF (monomer concentration is 0.0250 M).

by UV–Vis spectroscopy for unsubstituted monomers in methanol [21]. If the chlorine group is replaced by an iodine functionality (entry 4), polymerisation in methanol however occurs even without electron donors. This is a strong indication that in alcohols the expulsion of the leaving group is involved in the rate determing step of the reaction, the *p*-quinodimethane formation. However, not only the leaving group but also the substituents and type of solvent play a major role in the rate determing step. Electron donor substituents seem to enhance the rate of formation of the *p*-quinodimethane system probably because they facilitate the expulsion of the leaving group (e.g. entry 1).

Most striking however is the appearance of a bimodal molecular weight distribution for polymerisation reactions of unsubstituted and electron acceptor substituted monomers in aprotic solvents. Table 3 presents an overview of the influence of the solvent and substituents on the molecular weight distribution. High molecular weight polymers of unsubstituted PPV precursors are formed via a radical

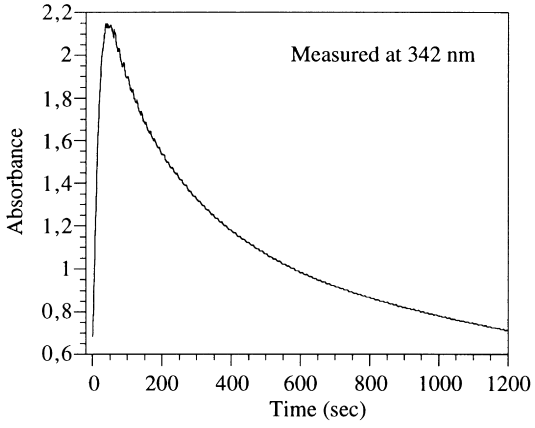
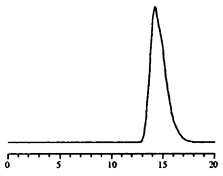
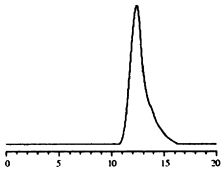
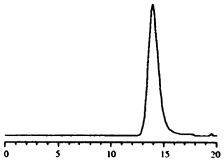
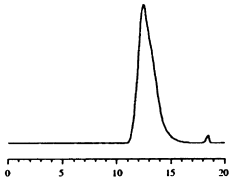
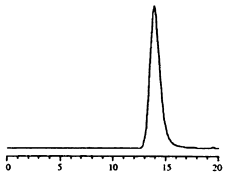
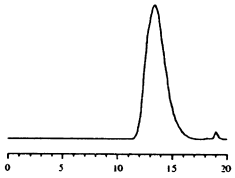
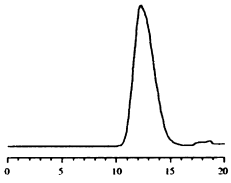
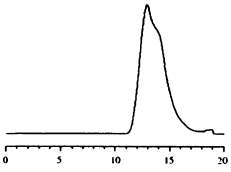
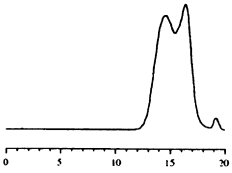
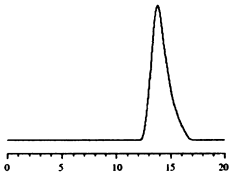
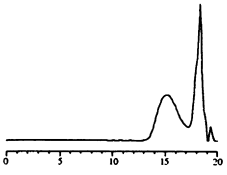
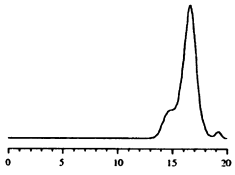


Fig. 3. UV–Vis visualisation of the formation and consumption of the *p*-quinodimethane intermediate for **1f** in THF (monomer concentration is 0.0025 M).

polymerisation as is demonstrated by addition of the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to the reaction mixture. Addition of 0.5 equiv of TEMPO to the reaction mixture in MMF (entry 7) totally inhibits the polymerisation reaction (entry 19). Similar results are even obtained in *s*-butanol, a solvent in which normally high polymer yields are obtained (entries 10 and 11) [21]. On the other hand, addition of TEMPO to the reaction mixture in NMP (entry 20), where normally a bimodal molecular weight distribution is observed (entry 17) [25], results in a monomodal distribution at the same elution time as the low molecular weight fraction of the standard bimodal distribution. TEMPO only inhibits the formation of the high molecular weight polymer. This points to a radical mechanism for the formation of the high molecular weight precursor polymers. The low molecular weight fraction seems to be formed by a non-radical mechanism. NMR studies have shown that in both cases a polymer with a similar structure is formed. Since aprotic solvents like NMP enhance the reactivity of the anions, an anionic mechanism is postulated for this kind of *p*-quinodimethane based polymerisations. Indeed, adding 5% (v/v) of water to the standard reaction mixture in NMP (entry 21) yields only the high molecular weight fraction while the formation of the low molecular weight fraction is blocked. This is confirmed by reactions in CH_2Cl_2, a solvent which is known to be unsuitable for anionic polymerisations [26]. Even with electron acceptors, a monomodal high molecular weight distribution is observed (entry 22).

In general, two polymerisation mechanisms can occur simultaneously: a radical mechanism that results in high molecular weight polymers and an anionic mechanism that yields low molecular weight polymers. The competition between both mechanisms however strongly depends on the reaction conditions, more specific on the solvent and monomer substituents. The anionic mechanism is not observed in protic solvents and is promoted by electron withdrawing

Table 3
Overview of the influence of the solvent and substituents on the formation and molecular weight distribution of precursor polymers (*x*-axes are given in minutes)

	Electron donors[a] (CH_3)	No substituents	Electron acceptors (Cl)
MeOH (protic polar)		No polymer formed	No polymer formed
MMF (protic polar)			No polymer formed
s-Butanol (protic apolar)			
THF (aprotic apolar)			
NMP (aprotic polar)			

[a] Electron donors are OMe functionalities.

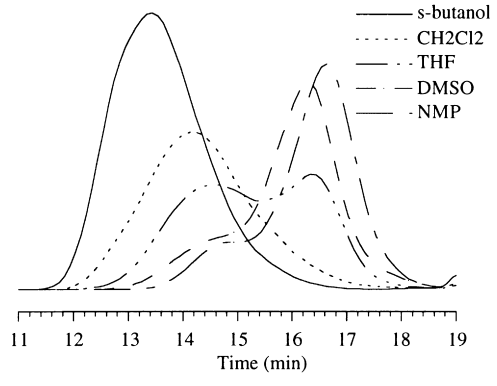


Fig. 4. Size exclusion chromatography of **3f** in various solvents.

substituents. Electron donor substituents on the other hand seem to suppress the anionic polymerisation. Protic solvents like MMF and alcohols seem to suppress the anionic mechanism which results in a monomodal molecular weight distribution independently of the type of substituent. In aprotic, apolar solvents like THF the anionic mechanism, and so bimodal distribution, is only observed in the absence of electron donors although it only becomes the main mechanism (low molecular weights) in the presence of electron acceptors. In aprotic, polar solvents like NMP and DMSO the anionic mechanism can only be suppressed if electron donors are present. Fig. 4 presents an overview of the molecular weight distribution of the precursor polymer

3f obtained in various solvents. A thorough discussion on the mechanism of the anionic polymerisation however is beyond the scope of this paper. Whether it concerns a chain- or step-growth process will be the subject of further work.

4. Conclusions

In this paper new insights in the mechanism of the sulfinyl precursor route towards PPV derivatives are presented by studying the polymerisation reaction in various solvents and by evaluating the influence of both electron donor and withdrawing substituents. A strong indication is presented that in alcohols the expulsion of the leaving group is involved in the rate determining step of the reaction, the formation of the *p*-quinodimethane intermediate. However, not only the leaving group but also the substituents and type of solvent play an important role in the rate-determing step. Electron donor substituents seem to enhance the rate of formation of the *p*-quinodimethane system probably because they facilitate the expulsion of the leaving group in the transition state.

Moreover, two polymerisation mechanisms can occur simultaneously: a radical mechanism which results in high molecular weight polymers and an anionic mechanism yielding low molecular weight polymers. The competition between both mechanisms however strongly depends on the solvent and type of substituents. Protic solvents clearly suppress the anionic mechanism. A bimodal molecular weight distribution is observed only for the polymerisation of unsubstituted and electron acceptor substituted monomers in aprotic solvents. The anionic mechanism is however clearly promoted by electron withdrawing substituents. Electron donor substituents seem to suppress the anionic polymerisation.

Acknowledgements

This study was performed as part of the program “Inter University Attraction Pole” (IUAP; contract P4/11) supported by the Belgian Government, Services of the Prime Minister—Federal Services for Scientific, Technical and Cultural affairs. The authors are grateful to the Flemish Institute for promotion of scientific and technological research in industry (IWT), the Fund for Scientific Research (FWO) and Hoechst AG for their financial support. Prof. R. Valcke and Prof. J. Vangronsveld are kindly acknowledged for making available the UV–Vis spectrophotometer. The authors also are grateful to Prof. G. Groeninckx and Dr G. Dreezen (KU Leuven) for the MDSC measurements.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. Nature 1990;347:539.
[2] Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed Engl 1998;37:402.
[3] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, dos Santos DA, Brédas JL, Lögdlund M, Salaneck WR. Nature 1999;397:121.
[4] Gilch HG, Wheelwright WL. J Polym Sci A-1 1966;4:1337.
[5] Wessling RA. J Polym Sci Polym Symp 1985;72:55.
[6] Son S, Lovinger AJ, Galvin ME. Polym Mater Sci Engng 1995;72:567.
[7] Son S, Dodabalapur A, Lovinger AJ, Galvin ME. Science 1995;269:376.
[8] Issaris A, Vanderzande D, Gelan J. Polymer 1997;38(10):2571.
[9] Van Der Borght M, Vanderzande D, Gelan J. Polymer 1998;39:4171.
[10] Vanderzande DJ, Issaris AC, Van Der Borght MJ, van Breemen AJ, de Kok MM, Gelan JM. Macromol Symp 1997;125:189.
[11] Lahti PM, Modarelli DA, Denton III FR, Lenz RW, Karasz FE. J Am Chem Soc 1988;110:7258.
[12] Garay R, Lenz RW. Makromol Chem 1989;5:1.
[13] Cho BR, Han MS, Suh YS, Oh KJ, Jeon SJ. J Chem Soc Chem Commun 1993:564.
[14] Denton III FR, Lahti PM, Karasz FE. J Polym Sci A: Polym Chem 1992;30:2223.
[15] Li I, Howell BA. Polym Prepr 1996;37:517.
[16] Salaneck WR, Brédas J-L. Adv Mater 1996;8(1):48.
[17] Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB. Nature 1993;365:628.
[18] Van Der Borght M, Vanderzande D, Adriaensens P, Gelan J. J Org Chem 2000, in press.
[19] Issaris A, Vanderzande D, Adriaensens P, Gelan J. Macromolecules 1998;31(14):4426.
[20] van Breemen AJJM, Vanderzande DJM, Adriaensens PJ, Gelan JMJV. J Org Chem 1999;64:3106.
[21] van Breemen AJJM, Issaris ACJ, de Kok MM, Van Der Borght MJAN, Adriaensens PJ, Gelan JMJV, Vanderzande DJM. Macromolecules 1999;32:5728.
[22] Massardier V, Beziat JC, Guyot A. Eur Polym J 1995;31(3):91.
[23] Cho BR, Kim YK, Han MS. Macromolecules 1998;31:2098.
[24] Hontis L, Van Der Borght M, Vanderzande D, Gelan J. Polymer 1999;40:6615.
[25] Louwet F, Vanderzande D, Gelan J. Synth Met 1996;69:509.
[26] Odian G. Principles of polymerization. 3rd edn. New York: Wiley, 1991.