

Precursor Route Chemistry and Electronic Properties of Poly(*p*-phenylenevinylene), Poly[(2,5-dimethyl-*p*-phenylene)vinylene] and Poly[(2,5-dimethoxy-*p*-phenylene)vinylene]

Paul L. Burn,^a Donal D. C. Bradley,^b Richard H. Friend,^b David A. Halliday,^b Andrew B. Holmes,^{a,*} Roger W. Jackson^a and Arno Kraft^a

^a University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

^b Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Several precursor polymer routes to poly(*p*-phenylenevinylene) **4**, poly[(2,5-dimethyl-*p*-phenylene)vinylene] **10** and poly[(2,5-dimethoxy-*p*-phenylene)vinylene] **15** are described. Base-induced polymerisation of bis-sulfonium salt monomers afforded the polyelectrolytes **3** and **9** which were converted respectively directly into either polymer **4** or **10**. Optimised conditions for the complete displacement of sulfonium groups by methanol to produce the corresponding methoxy precursor polymers **5**, **11** and **17** are reported. The fully conjugated polymers obtained after heat and acid treatment of these precursors have been characterised and compared with those obtained *via* different precursor routes. The ¹H NMR spectra of the precursor polymers, as well as IR and UV-VIS data of both the precursor polymers and the materials obtained after conversion into the poly(arylenevinylene)s are discussed.

In recent years there has been an increasing interest in the use of poly(arylenevinylene)s in opto-electronic applications such as electroluminescent devices.^{1,2} These applications demand materials of high purity, a condition which a number of synthetic routes developed so far have fulfilled only in part.³⁻⁸ A further goal is the modification of the basic poly(arylenevinylene)s to improve the electronic and structural properties and to vary aromatic ring substituents in order to control the π - π^* energy gap. Poly(arylenevinylene)s and oligomeric arylenevinylene⁹ are in most cases insoluble and unprocessable in aqueous or organic solvents and synthetic procedures have mostly involved the preparation of a precursor polymer which is processible, usually in solution, and which can then be converted into the desired poly(arylenevinylene); alternatively, these conjugated polymers can be rendered soluble and therefore processible in organic solvents by attaching large lipophilic groups to the arylenevinylene moiety.¹⁰⁻¹⁴ In this paper we describe our investigations with processible precursor polymers. The precursor route involves producing a polymer in which the arylene units are connected by ethylene units.³ The saturated units contain a group which not only solubilises the macromolecule and allows processing, but which can under suitable conditions also act as a leaving group, thus affording the unsaturated vinylene units of a fully conjugated polymer. We present in this paper a systematic study of the improved preparation of three poly(arylenevinylene)s, poly(*p*-phenylenevinylene) **4** (PPV), poly[(2,5-dimethyl-*p*-phenylene)vinylene] **10** (PDMePV) and poly[(2,5-dimethoxy-*p*-phenylene)vinylene] **15** (PDMeOPV); we discuss the reactivity of their precursor polymers and the influence of the synthetic pathway on the properties of the corresponding conjugated polymers.

Results and Discussion

General Characterisation Techniques.—All precursor polymers have been characterised by UV-VIS, IR and ¹H NMR spectroscopy. The UV-VIS spectra of the precursor polymers have mainly been used to determine the extent of conjugation which has been introduced into the polymer backbone during the polymerisation and processing. The IR spectra of these polymers have not only been employed to analyse whether any conjugation has been created during the polymerisation

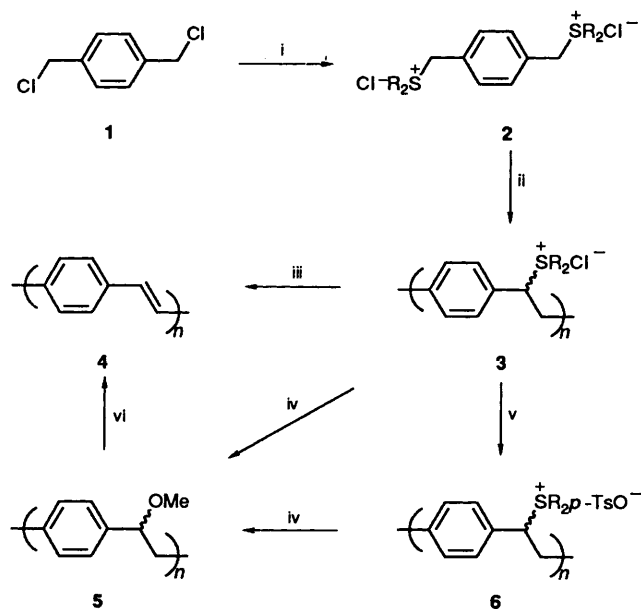
process, but also to follow the substitution reactions which have occurred on the polymer backbone. The ¹H NMR spectra can be complex but they do give important information about conjugated units and the relative proportions of leaving groups. The complexity arises from three main sources: firstly, due to the presence of the chiral centre at the benzylic carbon bearing the leaving group, the protons on the aromatic ring become non-equivalent in a number of cases, especially for the compounds in which the aromatic ring is substituted, and the two protons at the adjacent benzylic methylene group are diastereotopic; secondly, short relaxation times for the protons of the high molecular weight polymers give rise to broad signals ($T_{1\rho}\{^1\text{H}\}$ measurements on methanolic solutions of compound **3** [$R_2 = (\text{CH}_2)_4$] showed that the spin-lattice relaxation time of the aromatic protons is less than 0.13 s at room temperature); thirdly, considerable signal overlap occurs in the ¹H NMR spectra. Nevertheless, from chemical shift arguments the spectra can be assigned and valuable information on the degree of substitution of the leaving groups and the amount of conjugation in the polymer backbone can be ascertained.

The conjugated polymers have been characterised by UV-VIS absorption and IR spectroscopy.

Poly(*p*-phenylenevinylene) **4.**—PPV **4** is generally prepared by a polyelectrolyte precursor polymer route (Scheme 1) in which the charged species are sulfonium groups. The sulfonium groups solubilise the polymer in protic solvents such as water and methanol and, furthermore, they can be eliminated during the conversion into the conjugated polymer. A second precursor route where the solubilising and leaving group is an alkoxy group, usually methoxy, has been developed and gives polymers which are soluble in polar aprotic solvents such as chloroform, dichloromethane, and tetrahydrofuran (Scheme 1).⁸

We have shown that the different precursor polymers all give PPV. However, the structural and hence electronic properties can vary quite dramatically depending on which precursor polymer is utilised.^{19,20}

Some general remarks about the optimisation of the polymerisation procedure for the sulfonium precursor polymers can be made. For the preparation of the polymer we added aqueous sodium hydroxide to a methanolic solution of the chosen bis-sulfonium salt cooled in an ice-bath. We have



Scheme 1 Synthetic pathways to PPV 4. *Reagents and conditions:* i, Me_2S , $\text{S}[(\text{CH}_2)_3\text{CH}_2]$ or $\text{S}[(\text{CH}_2)_4\text{CH}_2]$, MeOH , 50°C [$\text{R} = \text{Me}$ or $\text{R}_2 = (\text{CH}_2)_4$ or $(\text{CH}_2)_5$]; ii, NaOH , $\text{MeOH-H}_2\text{O}$, 0°C ; iii, 220 or 300°C , vacuum; iv, MeOH , 52°C ; v, $p\text{-TsO}^-\text{Na}^+$; vi, 220°C , Ar-HCl

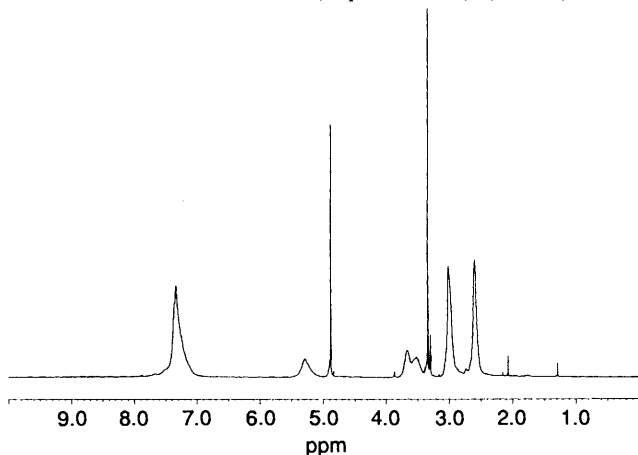


Fig. 1 ^1H NMR spectrum of polymer 3 ($\text{R} = \text{Me}$)

observed that if less than 1 mol equiv. of base, e.g. 0.9 mol equiv., is added slowly then the resultant polymer solution remains colourless. If 1 equiv. is used, then the resulting polymer solutions become coloured owing to base-induced elimination of some of the sulfonium groups, as the concentration of monomer units decreases the competing elimination reaction begins to dominate. This conjugation can be observed in the UV-VIS spectra of the precursor polymer. The polymerisations are terminated by addition of dilute hydrochloric acid to give a neutral or slightly acidic reaction mixture. Having a slight excess of acid at this stage is not harmful as it is removed in the purification step. However, by carefully neutralising the reaction mixture the amount of base consumed during the reaction can be determined and hence the extent of monomer consumed can be estimated. The polymer solutions were then dialysed against distilled water to remove the inorganic salts and low molecular weight material using dialysis tubing with a cut-off of 12 000 Da. The purified, mainly aqueous, polymer solutions can be used directly. However, we found that by removing the solvent and redissolving the residual polymer in methanol we could prepare thin films of higher quality than could be achieved with films spun from aqueous solutions. It was important that in this step the removal of the solvent was performed *in vacuo* at, or below, room temperature to prevent

elimination of the sulfonium groups. It was also advantageous to redissolve the dried precursor polymer immediately the solvent had been removed because the precursor polymers appear to eliminate sulfonium groups more rapidly in the solid state than they do in solution.

The use of a methanol-water mixture for the polymerisation reactions allowed us to prepare polymer 3 [$\text{R}_2 = (\text{CH}_2)_5$]. Although the synthesis of polymers 3 ($\text{R} = \text{Me}$) and 3 [$\text{R}_2 = (\text{CH}_2)_5$] have been reported in aqueous media, including the dialysis, the attempted preparation of 3 [$\text{R}_2 = (\text{CH}_2)_5$] under the same conditions was reported to have failed as the polymer formed a gel.⁵ By employing a water-methanol mixture during the polymerisation we showed that 3 [$\text{R}_2 = (\text{CH}_2)_5$] stayed in solution which was viscous and colourless. It was necessary to dialyse 3 [$\text{R}_2 = (\text{CH}_2)_5$] against methanol-water (1:1) because dialysis against distilled water caused the polymer to precipitate out of solution.

The UV-VIS spectra of the sulfonium precursor polymers 3 indicated that there was a small amount of conjugation present. The IR spectra did not show any special features and were often complicated by the presence of trapped methanol. The signals in the ^1H NMR spectra of the precursor polymers were broad and in each case integration revealed that there were relatively more aromatic and vinylic protons than would be expected compared with the aliphatic signals. We attribute this to the fact that some of the sulfonium groups had been eliminated. The diastereotopic protons form an interesting feature in all the ^1H NMR spectra of the precursor polymers. Polymer 3 ($\text{R} = \text{Me}$) has the methyl groups of the sulfonium salt in two different environments and the signals of the benzylic CH_2 protons are also split slightly (Fig. 1). With 3 [$\text{R}_2 = (\text{CH}_2)_4$] no splitting of the signals of the sulfonium methylene groups was observed; however, the benzylic methylene groups give rise to two types of signal. The CH_2 envelope for 3 [$\text{R}_2 = (\text{CH}_2)_5$] is much more complicated than the corresponding region in the NMR spectra of the dimethyl and tetrahydrothiophenium salt analogues, and specific assignment of the peaks is not possible.

Polymer 5 was first prepared by Tsutsui *et al.*⁷ who precipitated the sulfonium precursor polymer 3 [$\text{R}_2 = (\text{CH}_2)_4$] out of solution by exchanging the chloride anion with the toluene-*p*-sulfonate anion. They reported that on dissolution in methanol the resultant polymer would react with methanol at room temperature to give polymer 5. The reaction at this temperature appeared to be extremely sluggish. However, as we have recently reported,⁸ the reaction proceeds much more rapidly by heating the methanolic solution of 3 [$\text{R}_2 = (\text{CH}_2)_4$] (42°C overnight followed by 26 h at 52°C). This reaction should be independent of the counteranion. Thus we have found that 5 could be prepared directly from a methanolic solution of 3 [$\text{R}_2 = (\text{CH}_2)_4$] by heating at 42°C overnight followed by 26 h at 52°C . Full conversion into the methoxy leaving-group precursor polymer was evidenced by both IR and ^1H NMR spectroscopy. The resulting polymer is amenable to GPC analysis and exhibits molecular weight averages similar to those reported for analogous thiophenoxy-substituted polymers.²¹ As in the case of the polymers 3 the NMR spectrum of polymer 5 shows splitting of the benzylic CH_2 signals indicating the presence of the adjoining chiral centre. In both precursor polymer routes (sulfonium and methoxy) there is evidence for some elimination of the leaving groups, either the sulfonium leaving group by thermal elimination, or the methoxy leaving group by thermal elimination under acid catalysis. The elimination of sulfonium leaving groups produces hydrogen chloride as a by-product. This can in turn promote elimination of methoxy leaving groups. The conjugation can be seen both in the IR (Fig. 2) and ^1H NMR (Fig. 3) spectra by a decrease in the signal due to the methoxy leaving group and an increase in the signals due to the conjugated units.

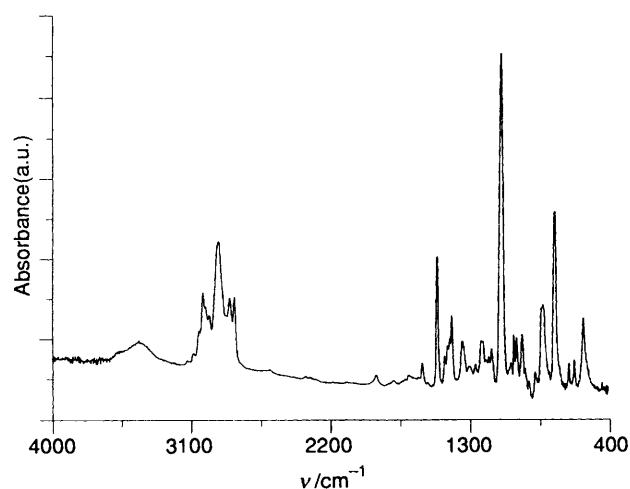


Fig. 2 IR spectrum of polymer 5 showing the signals due to the methoxy leaving group (1097 cm^{-1}) and unsaturated units (965 cm^{-1})

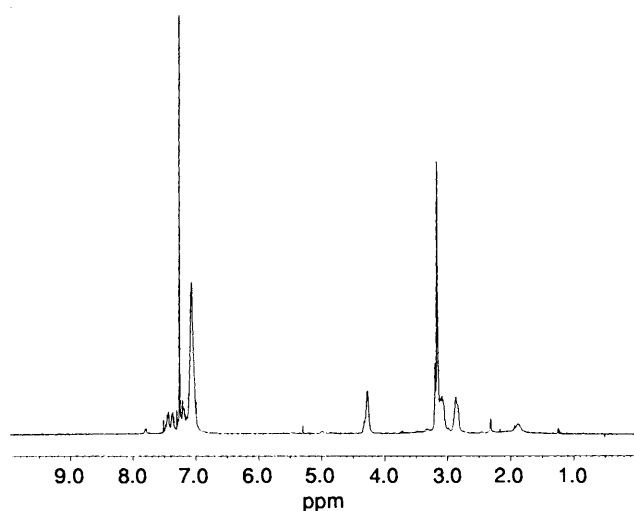


Fig. 3 ^1H NMR spectrum of polymer 5 showing signals at δ 3.19, 3.32, 4.96, 7.37 and 7.44 with relatively increased intensity according to the presence of greater amounts of conjugated units

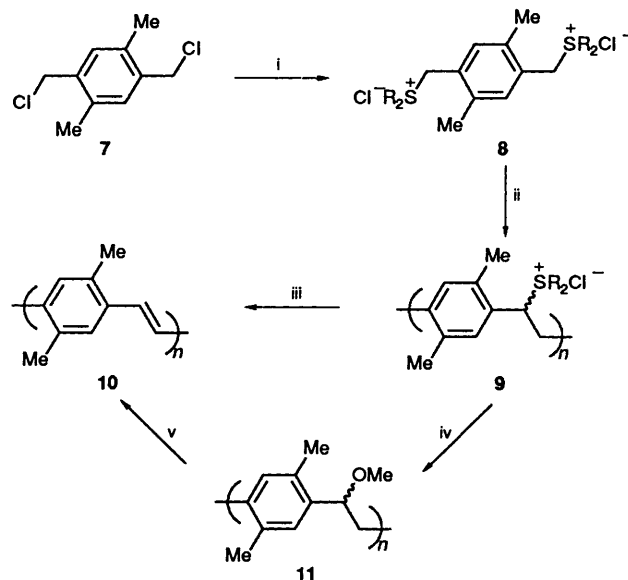
Precursor polymer 3 [$\text{R}_2 = (\text{CH}_2)_4$] can be stored as a methanolic solution at -20°C ; under these conditions the tetrahydrothiophenium groups appear to be stable against substitution by methanol even after several months.

The sulfonium group precursor polymers were converted into the conjugated polymers by heating thin films at typically $220\text{--}250^\circ\text{C}$ for 12 h under vacuum. Combustion microanalysis of PPV formed from 3 [$\text{R}_2 = (\text{CH}_2)_4$, $(\text{CH}_2)_5$] indicated the absence of residual sulfur, while that formed by heating 3 ($\text{R} = \text{Me}$) for 12 h at 300°C exhibited the presence of residual sulfur (8.3%). Polymers 3 [$\text{R}_2 = (\text{CH}_2)_4$ and $(\text{CH}_2)_5$] give rise to PPV with similar band-edge energies (defined arbitrarily as the half height maximum of the absorption peak of lowest energy). These values are red-shifted compared with the band-edge energy of PPV prepared from 3 ($\text{R} = \text{Me}$), consistent with the presence of residual MeS groups in the polymer. They also exhibit more vibrational structure. The reasoning behind this is reported by us and others elsewhere.^{8,17,19}

Heat treatment of polymer 5 gave rise to a thermally stable partially conjugated precursor polymer.²² To prepare the fully conjugated PPV it was necessary to heat the precursor polymer at 200°C under flowing hydrogen chloride–argon. This led to PPV with a similar band-edge energy to PPV prepared *via* 3 [$\text{R}_2 = (\text{CH}_2)_4$ and $(\text{CH}_2)_5$], but with little vibrational

structure. Small variations in band-edge energies may be due to slight differences in film thicknesses.

Poly[(2,5-dimethyl-p-phenylene)vinylene] 10.—Iodine-doped PDMePV has previously been reported by Antoun *et al.*⁴ We have obtained PDMePV from both sulfonium and methoxy leaving group precursor polymers (Scheme 2). As expected on



Scheme 2 Synthetic pathways to PDMePV 10. Reagents and conditions: i, $\text{S}[(\text{CH}_2)_3\text{CH}_2]$, MeOH, 55°C [$\text{R}_2 = (\text{CH}_2)_4$]; ii, NaOH, MeOH– H_2O , 0°C ; iii, 220°C , vacuum; iv, MeOH, 52°C ; v, 220°C , Ar–HCl

electronic grounds (the two methyl groups on the aromatic ring are inductively electron-donating) we observe that the reactivity of the precursors to PDMePV are indeed intermediate in reactivity between those for PPV and PDMeOPV 15 which will be discussed later.

The sulfonium precursor to PDMePV was prepared in a similar fashion to the sulfonium precursors to PPV. A methanolic solution of the bis-sulfonium salt 8 [$\text{R}_2 = (\text{CH}_2)_4$] was treated with just under 1 mol equiv. of aqueous base. The reaction was terminated by addition of hydrochloric acid and the resultant polymer was then purified by dialysis against distilled water. After removal of the solvent, the residue 9 was dissolved in methanol for processing. However, unlike the sulfonium precursor polymers to PPV some reaction of 9 with methanol took place. The methyl groups on the aromatic rings activate the benzylic carbons which contain the sulfonium groups towards nucleophilic substitution. This activation is not as great as in the case of the PDMeOPV precursor polymers where substitution occurred predominantly within the first 20 min at room temperature, as indicated by the precipitation of the polymer 17, the methoxy leaving-group precursor polymer of PDMeOPV (see below). Evidence for the substitution of some of the sulfonium groups with methanol comes from the IR spectrum, the subsequent chemistry which polymer 10 undergoes, and the ^1H NMR spectrum. In carefully dried films of polymer 9 there is an IR absorption at 1098 cm^{-1} corresponding to the C–O stretch of the methoxy group. This was determined by comparison with the IR spectrum of polymer 11, the methoxy leaving-group precursor polymer to PDMePV 10. On thermal treatment, elimination of the sulfonium groups and hydrogen chloride occurred and polymer 9 became more conjugated as indicated by a change in colour and the absorption spectrum. Also the combustion microanalysis revealed the absence of residual sulfur in the film. However, a

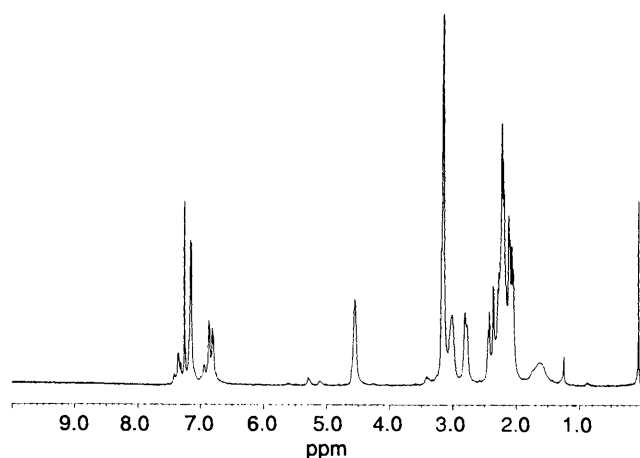
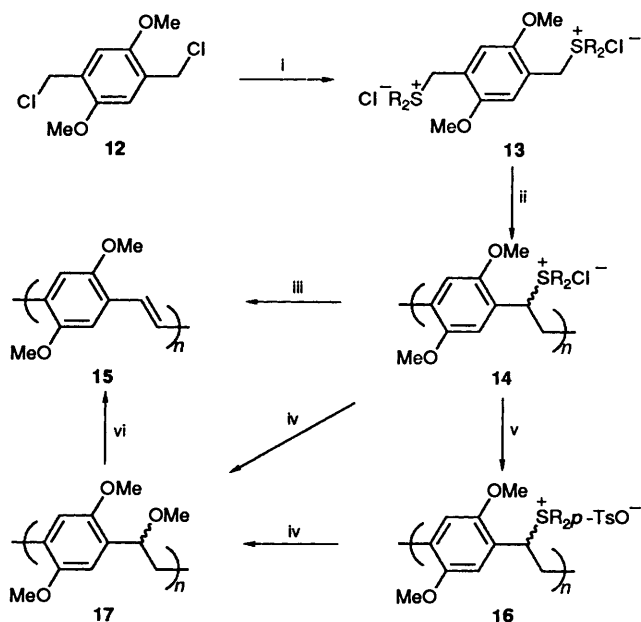


Fig. 4 ^1H NMR spectrum of polymer 11

significant number of methoxy leaving groups remained, as evidenced by the residual peak at 1098 cm^{-1} in the IR spectrum. The fully conjugated PDMePV 10 was obtained from polymer 9 by treatment at 200°C with a constant flow of hydrogen chloride–argon. This caused a further red-shift of the band-edge energy of 0.02 eV and the IR spectrum of the resultant material became identical with that of polymer 10 prepared *via* polymer 11.

The methoxy precursor polymer 11 is prepared directly from compound 9 by taking a dilute solution of the sulfonium precursor polymer in methanol and heating it at 50°C overnight. Conversion of 9 into 11 is evidenced from both the IR and ^1H NMR spectra. The ^1H NMR spectrum shows signals at δ 3.14 and 4.54 which according to chemical shift arguments correspond to the methoxy leaving groups and the methine protons respectively (Fig. 4). Polymer 11 is then converted into the fully conjugated polymer 10 by thermal treatment under acidic conditions as described for 9. The fact that all these materials have band-edge energies greater than PPV is thought to be due to the steric inhibition of planarity arising from allylic strain caused by the aromatic methyl substituents. Similar effects on the coplanarity of a copolymer derived from PPV and poly[(2,3,5,6-tetramethyl-*p*-phenylene)vinylene] have previously been noted.²³

Poly[(2,5-dimethoxy-*p*-phenylene)vinylene] 15.—The chemistry involved in the preparation of PDMeOPV is governed by the increased reactivity of the intermediates due to the two methoxy groups attached to the aromatic ring (Scheme 3). The bis-sulfonium salt monomer 13 was prepared by a literature method,¹⁷ but appears to decompose, in contrast to the PPV monomer which is stable for months. This is probably due to the two methoxy groups on the benzene ring activating the benzylic positions towards substitution by nucleophiles such as water or chloride. It has been shown that the sulfonium precursor polymer 14 to PDMeOPV is unstable in aqueous solution and undergoes reaction with water to give a precursor whose sulfonium groups are, at least in part, substituted by hydroxy groups.^{7,8,22} This material is insoluble in water and organic solvents, hence unprocessable, and currently of no use. This reactivity of the benzylic position can be utilised advantageously by taking an aqueous solution of the sulfonium precursor polymer and exchanging the chloride anion with the toluene-*p*-sulfonate anion as in the preparation of 5. The material 16 forms a yellowish gum which is soluble in methanol.²⁴ Unlike the PPV precursor polymer the methanol substitution reaction required no heating and the sulfonium precursor polymer underwent substitution at room temper-



Scheme 3 Synthetic pathways to PDMeOPV 15. Reagents and conditions: i, $\text{S}[\text{CH}_2]_3\text{CH}_2$, MeOH, 50°C [$\text{R}_2 = (\text{CH}_2)_4$]; ii, NaOH, H_2O , 0°C or $[\text{Bu}_4\text{N}]^+ \text{OH}^-$, MeOH, 0°C ; iii, 300°C , vacuum; iv, MeOH, 25°C ; v, *p*-TsO⁻Na⁺; vi, 200°C , Ar–HCl.

ature. An initial precipitate was often observed after *ca.* 20 min, but for the reaction to go to completion it is best to leave it for 16 h. This resulted in polymer 17 as a gelatinous whitish precipitate which could be filtered, air-dried, and dissolved in polar aprotic organic solvents. We have shown that it is not necessary to exchange the chloride anion with the toluene-*p*-sulfonate anion for this reaction to occur. Simply by taking an aqueous solution of the sulfonium precursor polymer and removing the solvent followed by dissolution in methanol the same reaction as above took place yielding polymer 17 as a precipitate.

The disadvantages of these two processes are twofold. The number of steps in both treatments take not only extra time but they also give rise to a possible new problem. It has been noted that in the synthesis of the methoxy leaving-group precursor polymer to poly(2,5-thiylenevinylene) the sulfonium group can also be substituted by water.²⁵ The proportion of hydroxy groups present then governs the solubility of the precursor polymer, *i.e.*, the more hydroxy groups present, the less soluble the precursor polymer will be. To avoid the possibility of this undesired side-reaction occurring with the sulfonium precursor to PDMeOPV it is necessary to eliminate water as a component of the reaction. By employing methanolic tetrabutylammonium hydroxide as the base and conducting the polymerisation in dry methanol at 0°C we have shown that the sulfonium precursor polymer 14 can be easily prepared. Simply leaving the acid-quenched reaction mixture at room temperature for *ca.* 16 h allowed a one-pot synthesis of 17.

Complete substitution of the sulfonium groups with methanol is evidenced from both the IR and ^1H NMR spectra. The IR spectrum shows a strong absorption due to the asymmetric C–O–C stretch of the CHOCH_3 units and no absorptions due to any sulfonium substituents. The ^1H NMR spectrum has signals at δ 3.20 and 4.86 corresponding to the methoxy leaving group and the methine protons respectively (Fig. 5). There are no signals for residual sulfonium groups observed.

As in the case of 5 and 11 it was necessary to treat 17 thermally under acidic conditions in order to obtain conjugated polymers. The reaction conditions are 200°C , under a con-

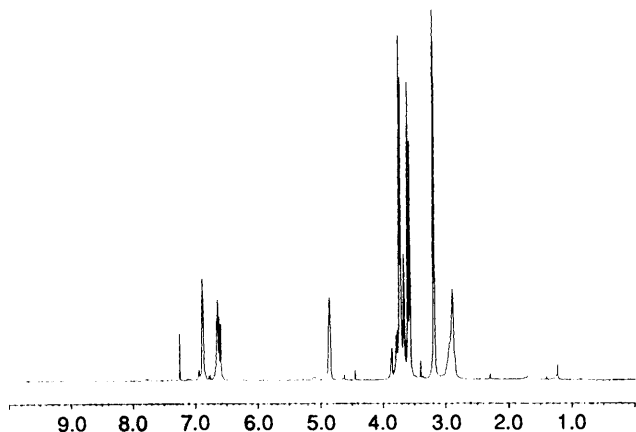


Fig. 5 ^1H NMR spectrum of polymer 17

stant flow of argon–hydrogen chloride mixture for 2 h. The conversion into the fully conjugated material can be followed in the IR spectrum by the disappearance of the methoxy leaving group stretch at 1093 cm^{-1} and the corresponding red-shift of the band-edge energy to 2.34 eV in the absorption spectrum. This should be contrasted with the onset for the absorption band which is 2.1 eV. Clearly the exact position of the band edge will be dependent on a number of factors including the nature of the precursor polymer.²⁶

Experimental

Reagents.—Methanol was dried and purified by distillation from magnesium methoxide.¹⁵ Distilled water was used in the reactions and the aqueous sodium hydroxide and hydrochloric acid solutions were freshly prepared for each reaction.

Measurements.—NMR spectra were recorded on Bruker WM-400 or WP-80-SY spectrometers with tetramethylsilane as internal reference. ^{13}C NMR spectra were fully decoupled. IR spectra of polymers were recorded on a Nicolet 5SXB FTIR spectrometer either as free standing films or as films on pressed potassium bromide discs. UV–VIS spectra were recorded as spun films either on glass or Spectrosil substrates on a Perkin-Elmer Lambda 9 instrument. The band-edge is defined as the half height maximum of the absorption peak of lowest energy (longest wavelength). This is an arbitrary definition (it does not correspond to a particular electronic transition) which allows different materials to be compared easily. Gel permeation chromatography separations of methoxy-substituted precursor polymers were carried out with a Polymer Laboratories PLgel 5 μm MIXED-C column (300 mm length) calibrated with polystyrene narrow standards (mass range 1 130 000–580) in chloroform with toluene as flow marker. The chloroform solvent was pumped at 5 MPa at a flow rate of $10\text{ cm}^3\text{ min}^{-1}$ at $30\text{ }^\circ\text{C}$ and the UV detector was set at 260 nm. Spin-coated samples were typically prepared by covering a substrate with a solution of the precursor polymer and spinning this at 2000 revolutions per min for 60 s on a Dynapert PRS14E spinner for photoresists, the solvent being allowed to evaporate under ambient conditions. The precursor films (spun or free cast) were converted into conjugated materials either by thermal treatment under a dynamic vacuum or by thermal treatment under a constant flow of a mixture of hydrogen chloride and argon. The thicknesses of films produced using these conditions were in the range of 60–100 nm after conversion from the precursor polymers. Such films provide optical densities at the peak of the π – π^* absorption maximum in the range 1–3. M.p.s were determined using a Büchi 510 m.p. apparatus. Microanalyses were determined by Mr. D. Flory and staff at the University Chemical Laboratory.

Synthesis.—All polymerisations were carried out under nitrogen or argon. For dialysis a cellulose membrane dialysis tubing with a molecular weight cut-off of 12 400 Da (supplied by Sigma Chemical Company Limited, Dorset, UK) was used. All precursor polymers were stored in solution (methanol for the sulfonium salts, dichloromethane for the methoxy-substituted polymers) at $-15\text{ }^\circ\text{C}$. Deuteriated chloroform was the preferred solvent for NMR studies of the methoxy-substituted polymers, but elimination occurred more readily in this solvent, hence they were stored in dichloromethane.

Poly(*p*-phenylenevinylene) 4

***p*-Phenylenedimethylene-1,1'-bis(thian-1-ium) Dichloride 2** [$\text{R}_2 = (\text{CH}_2)_5$].—A mixture of α,α' -dichloro-*p*-xylene (2.01 g, 11.5 mmol) and thiane (6.0 cm^3 , 60 mmol) in methanol (50 cm^3) was stirred at $50\text{ }^\circ\text{C}$ under argon for 19 h. The reaction mixture was allowed to cool to room temperature, and then poured onto dry acetone (300 cm^3) and filtered and dried thoroughly *in vacuo* to yield the title salt 2 [$\text{R} = (\text{CH}_2)_5$] (2.44 g, 56%), a colourless solid, m.p. 169 – $173\text{ }^\circ\text{C}$ (decomp); δ_{H} (400 MHz; CD_3OD) 1.71 (2 H, m, CH_2), 1.87 (6 H, m, CH_2), 2.28 (4 H, m, CH_2), 3.30 (4 H, m, SCH_2), 3.52 (4 H, m, SCH_2), 4.84 (4 H, s, benzylic CH_2) and 7.65 (4 H, s, ArH); δ_{C} (100.6 MHz; CD_3OD) 22.5, 23.8, 37.2, 44.5, 130.9 and 132.8.

Route 1. Via Sulfonium Precursor Polymers.—Poly{*p*-phenylene[1-(dimethylsulfonio)ethylene chloride]} 3 ($\text{R} = \text{Me}$). To a solution of *p*-phenylenedimethylene-1,1'-bis(dimethylsulfonio) dichloride 2 ($\text{R} = \text{Me}$)¹⁶ (1.0 g, 3.3 mmol) in methanol (9 cm^3) cooled to $0\text{ }^\circ\text{C}$ was added dropwise aqueous sodium hydroxide (0.4 mol dm^{-3} ; 8.8 cm^3 , 3.5 mmol) over 20 min. The reaction mixture was stirred for a further 60 min at $0\text{ }^\circ\text{C}$ and neutralised with hydrochloric acid (0.4 mol dm^{-3}). The solution was then dialysed against water over 3 days ($3 \times 1000\text{ cm}^3$) after which the solvent was completely removed. The residue ($\approx 0.20\text{ g}$) was redissolved in methanol (4.0 cm^3); δ_{H} (400 MHz; CD_3OD) 2.62 (br s, CH_3), 3.02 (br s, CH_3), 3.53 (br s, benzylic CH_2), 3.69 (br s, benzylic CH_2), 5.26 (br s, CH) and 7.32 (br m, ArH and conjugated unit H).

Poly{*p*-phenylene[1-(tetrahydrothiophen-1-*io*)ethylene chloride]} 3 [$\text{R}_2 = (\text{CH}_2)_4$]. To a solution of *p*-phenylenedimethylene-1,1'-bis(tetrahydrothiophen-1-ium) dichloride 2 [$\text{R}_2 = (\text{CH}_2)_4$]¹⁷ (5.0 g, 14 mmol) in methanol (38 cm^3) cooled to $0\text{ }^\circ\text{C}$ was added dropwise aqueous sodium hydroxide (0.4 mol dm^{-3} ; 36 cm^3 , 14 mmol) over 20 min. The reaction mixture was stirred for a further 60 min at $0\text{ }^\circ\text{C}$ and then neutralised with hydrochloric acid (0.4 mol dm^{-3}). The solution was then dialysed against water over 3 days ($3 \times 2000\text{ cm}^3$) after which the solvent was completely removed. The residue ($\approx 1.3\text{ g}$) was redissolved in methanol (75 cm^3); δ_{H} (400 MHz; CD_3OD) 2.08 (br m, CH_2), 2.92 (br s, benzylic CH_2), 3.31 (br s, benzylic CH_2), 3.63 (br m, SCH_2), 5.05 (br s, CH) and 7.35 (br m, ArH and conjugated unit H).

Poly{*p*-phenylene[1-(tetrahydrothiophen-1-*io*)ethylene chloride]} 3 [$\text{R}_2 = (\text{CH}_2)_5$]. To a solution of the salt 2 [$\text{R}_2 = (\text{CH}_2)_5$] (1.0 g, 2.6 mmol) in methanol (7.5 cm^3) cooled to $0\text{ }^\circ\text{C}$ was added dropwise aqueous sodium hydroxide (0.4 mol dm^{-3} ; 6.3 cm^3 , 2.5 mmol). The reaction mixture was stirred for a further 120 min at $0\text{ }^\circ\text{C}$ and slightly acidified with hydrochloric acid (0.4 mol dm^{-3} ; 1.0 cm^3). The solution was then dialysed against a water–methanol mixture (1:1, $3 \times 1000\text{ cm}^3$) over 3 days after which the solvent was completely removed. The residue was redissolved in methanol (15 cm^3); δ_{H} (400 MHz; CD_3OD) 1.62, 1.85, 2.20, 2.33, 2.85, 2.96, 3.49, 3.67 and 3.79 (br s, CH_2 , benzylic CH_2 and SCH_2), 5.36 (br s, CH) and 7.36 (br m, ArH and conjugated unit H).

Thermal conversion of polymer 3 ($\text{R} = \text{Me}$) into polymer 4.

Thin films of the polymer **3** ($R = \text{Me}$) were heated at 300 °C for 12 h *in vacuo* to form the polymer **4**; $\nu_{\text{max}}/\text{cm}^{-1}$ 3026, 1519, 1424, 963, 837 and 558; $\lambda_{\text{max}}/\text{nm}$ 405, 247 and 191; band-edge energy 2.53 eV (Found: S, 8.3%).

Thermal conversion of polymer 3 [$R_2 = (\text{CH}_2)_4$] into polymer **4**. Thin films of the polymer **3** [$R_2 = (\text{CH}_2)_4$] were heated at 220 °C for 12 h *in vacuo* to form the polymer **4** which had peaks in positions identical with those in the IR spectrum of the material prepared from **3** ($R = \text{Me}$); $\lambda_{\text{max}}/\text{nm}$ 427, 258 and 200; band-edge energy 2.49 eV.

Thermal conversion of polymer 3 [$R_2 = (\text{CH}_2)_5$] into polymer **4**. Thin films of the polymer **3** [$R_2 = (\text{CH}_2)_5$] were heated at 220 °C for 12 h *in vacuo* to form the polymer **4** which had peaks in positions identical with those in the IR spectrum of the material prepared from **3** ($R = \text{Me}$); $\lambda_{\text{max}}/\text{nm}$ 432, 258 and 205; band-edge energy 2.46 eV.

Route 2. Via a Methoxy Precursor Polymer.—Poly[*p*-phenylene(1-methoxyethylene)] **5**. **Method 1**. To a solution of the salt **2** [$R_2 = (\text{CH}_2)_4$]¹⁷ (1.0 g, 2.9 mmol) in water (28 cm³) cooled to 0 °C was added dropwise aqueous sodium hydroxide (0.4 mol dm⁻³; 7.1 cm³, 2.8 mmol). The reaction mixture was stirred for a further 60 min at 0 °C and then quenched with hydrochloric acid (0.4 mol dm⁻³; 4 cm³). To the solution was added sodium toluene-*p*-sulfonate (1.9 g, 9.8 mmol) and the mixture was stirred for a further 15 min. The aqueous layer was decanted from the gummy residue which was washed with water (25 cm³). The residue was dissolved in methanol (25 cm³) and then stirred at 42 °C overnight followed by stirring at 52 °C for 26 h. The colourless precipitate that formed was filtered off and washed well with methanol. It was then dissolved in dichloromethane after which the solvent was completely removed. The residue, the polymer **5**, was dissolved in chloroform to give a saturated solution; δ_{H} (400 MHz; CDCl₃) 2.85 (br s, benzylic CH₂), 3.00–3.57 (br m, OCH₃ and benzylic CH₂), 4.28 (br s, CH), 4.96 (br s, CH), 7.07 (br s, ArH) and 7.20, 7.37 and 7.44 (br m, conjugated unit H); $\nu_{\text{max}}/\text{cm}^{-1}$ 3008, 2940, 2849, 2821, 1512, 1097 (CHOCH₃), 841, 819 and 571.

Method 2. A methanolic solution of polymer **3** [$R_2 = (\text{CH}_2)_4$] ($\approx 17 \text{ mg cm}^{-3}$; 10 cm³) was added to methanol (100 cm³) and the solution was stirred at 55 °C for 16 h. The precipitate was filtered off, washed with methanol (100 cm³) and then air-dried. The residue **5** was dissolved in chloroform. This material had peaks in positions identical with those in the IR and ¹H NMR spectra of the material prepared in route 1.

A similar experiment with polymer **3** [$R_2 = (\text{CH}_2)_4$] prepared by addition of base over 20 min and further polymerisation over 40 min afforded the methoxy-substituted polymer **5** which was analysed by GPC, M_n 9.75 × 10⁴; M_w 5.6 × 10⁵; polydispersity index 5.7.

Acid and thermal conversion of polymer 5 into polymer 4. Thin films of the polymer **5** were heated at 220 °C for 12 h under a hydrogen chloride–argon flow to form the polymer **4**. This material had peaks in positions identical with those in the IR spectrum of the material prepared from **3**; $\lambda_{\text{max}}/\text{nm}$ 456, 262 and 205; band-edge energy 2.42 eV.

Poly[2,5-dimethyl-*p*-phenylene]vinylene] **10**

2,5-Dimethyl-*p*-phenylenedimethylene-1,1'-bis(tetrahydrothiophen-1-ium) Dichloride 8 [$R_2 = (\text{CH}_2)_4$].—A mixture of 1,4-bis(chloromethyl)-2,5-dimethylbenzene **7**¹⁸ (2.45 g, 12.1 mmol) and tetrahydrothiophene (8.5 cm³, 96 mmol) in methanol (17 cm³) was stirred at 55 °C for 48 h. The reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure, and poured into ice-cold acetone (100 cm³).

The precipitate was filtered off, washed with dry acetone, and then dried thoroughly *in vacuo* to yield the title monomer **8** [$R_2 = (\text{CH}_2)_4$] (4.16 g, 91%), a colourless solid, m.p. 147–149 °C; δ_{H} (80 MHz; CD₃OD) 2.17–2.64 (8 H, m, CH₂), 2.50 (6 H, s, CH₃), 3.43–3.68 (8 H, m, SCH₂), 4.76 (4 H, s, benzylic CH₂) and 7.49 (2 H, s, ArH).

Poly{2,5-dimethyl-*p*-phenylene[1-(tetrahydrothiophen-1-ium)-ethylene chloride]} **9** [$R_2 = (\text{CH}_2)_4$].—To a solution of the salt **8** (0.60 g, 1.6 mmol) in methanol (16 cm³) cooled to 0 °C was added dropwise aqueous sodium hydroxide (0.4 mol dm⁻³; 4.0 cm³, 1.6 mmol) over 20 min. The reaction mixture was stirred for a further 60 min at 0 °C and neutralised with hydrochloric acid (0.4 mol dm⁻³; 0.3 cm³). The viscous solution was then dialysed against water over 3 days (3 × 1000 cm³) after which the solvent was completely removed. The residue, polymer **9** [$R_2 = (\text{CH}_2)_4$] ($\approx 0.10 \text{ g}$), was redissolved in methanol (9 cm³); δ_{H} (400 MHz; CD₃OD) 1.78–2.31 (br m, CH₂ and CH₃), 2.50–3.78 (br m, CH₂ and OCH₃), 4.26, 4.53, 4.87 and 5.31 (br s, CH) and 6.70–7.44 (br m, ArH and conjugated unit H); $\nu_{\text{max}}/\text{cm}^{-1}$ 3009, 2948, 2921, 2867, 1503, 1449, 1098 (CHOCH₃), 1036 and 893.

Thermal conversion of polymer 9 [$R_2 = (\text{CH}_2)_4$] into the polymer **10**. Thin films of polymer **9** [$R_2 = (\text{CH}_2)_4$] were heated at 220 °C for 12 h *in vacuo* to form the polymer **10**; $\nu_{\text{max}}/\text{cm}^{-1}$ 3048, 3014, 2964, 2942, 2921, 2861, 1503, 1459, 1098 (CHOCH₃), 961 and 882; $\lambda_{\text{max}}/\text{nm}$ 393, 247sh and 208; band-edge energy 2.73 eV.

Acid and thermal conversion of polymer 9 [$R_2 = (\text{CH}_2)_4$] into polymer **10**. Thin films of polymer **9** [$R_2 = (\text{CH}_2)_4$] were heated at 220 °C for 12 h under a hydrogen chloride–argon flow to form the polymer **10**; $\nu_{\text{max}}/\text{cm}^{-1}$ 3045, 3014, 2966, 2945, 2921, 2867, 1505, 1457, 963 and 882; $\lambda_{\text{max}}/\text{nm}$ 395, 248sh and 210; band-edge energy 2.71 eV.

Poly[(2,5-dimethyl-*p*-phenylene)(1-methoxyethylene)] 11.—A solution of polymer **9** [$R_2 = (\text{CH}_2)_4$] ($\approx 0.5 \text{ mg cm}^{-3}$; 100 cm³) in methanol was heated at 50 °C for 12 h. The reaction mixture was filtered and the title polymer **11** ($\approx 30 \text{ mg}$), a colourless gelatinous solid, was redissolved in dry chloroform (5 cm³); δ_{H} (400 MHz; CDCl₃) 2.04–2.44 (br m, PhCH₃), 2.80 (br s, benzylic CH₂), 3.01 (br s, benzylic CH₂), 3.14 (br s, OCH₃), 4.54 (br s, CH), 7.15, 6.78–6.95 and 7.31–7.42 (br m, ArH and conjugated unit H); $\nu_{\text{max}}/\text{cm}^{-1}$ 2925, 2819, 1503, 1457, 1098 (CHOCH₃) and 756.

Acid and thermal conversion of polymer 11 into the polymer 10. Thin films of polymer **11** were heated at 220 °C for 12 h under a hydrogen chloride–argon flow to form polymer **10** which had peaks in positions identical with those in the spectrum of the material prepared from **9** on acid and thermal treatment; $\lambda_{\text{max}}/\text{nm}$ 396, 254sh and 214; band-edge energy 2.66 eV.

Poly[(2,5-dimethoxy-1,4-phenylene)vinylene] **15**

Poly[(2,5-dimethoxy-*p*-phenylene)-(1-methoxyethylene)]

17.—**Method 1**. To a solution of 2,5-dimethoxy-*p*-phenylenedimethylene-1,1'-bis(tetrahydrothiophen-1-ium) dichloride **13** [$R_2 = (\text{CH}_2)_4$]¹⁷ (2.0 g, 4.9 mmol), in water (15 cm³) cooled to 0 °C was added dropwise aqueous sodium hydroxide (0.4 mol dm⁻³; 15 cm³, 6.0 mmol) over 30 min. The reaction mixture was stirred for a further 2 h at 0 °C and then quenched with hydrochloric acid (0.4 mol dm⁻³; 0.8 cm³). To this solution was added dropwise aqueous sodium toluene-*p*-sulfonate (0.4 mol dm⁻³; 30 cm³). The reaction mixture was stirred at room temperature for 30 min and the solvent was decanted. Dry methanol (100 cm³) was added and the reaction mixture was stirred at room temperature for 12 h. The mixture was filtered and the residue washed with dry methanol (50 cm³) and then air-dried. The residue, polymer **17** ($\approx 125 \text{ mg}$), was dissolved in

dichloromethane (3.5 cm³); δ_{H} (400 MHz; CDCl₃) 2.90 (br s, benzylic CH₂), 3.20 and 3.24 (br s, OCH₃), 3.59–3.76 (br m, ArOCH₃), 4.87 (br s, CH), and 6.63 and 6.89 (br m, ArH); $\nu_{\text{max}}/\text{cm}^{-1}$ 2933, 2831, 1503, 1465, 1405, 1358, 1218, 1094 (CHOCH₃) and 1050.

Method 2. To a solution of the salt **13** [$\text{R}_2 = (\text{CH}_2)_4$]¹⁷ (2.0 g, 4.9 mmol), in water (15 cm³) cooled to 0 °C was added dropwise aqueous sodium hydroxide (0.4 mol dm⁻³; 15 cm³, 6.0 mmol) over 30 min. The reaction mixture was stirred for a further 2 h at 0 °C and then quenched with hydrochloric acid (0.4 mol dm⁻³; 0.7 cm³). The solvent was completely removed and the residue was redissolved in dry methanol (100 cm³). The reaction mixture was stirred for 12 h at room temperature, filtered and the residue was washed with dry methanol (50 cm³) and then air-dried at the filter. The residue, polymer **17** (\approx 140 mg), was dissolved in dichloromethane (3.5 cm³). This material had IR and ¹H NMR spectra identical with those from the material formed in method 1.

Method 3. To a solution of the salt **13** [$\text{R}_2 = (\text{CH}_2)_4$]¹⁷ (8.84 g, 21.5 mmol), in methanol (60 cm³) cooled to 0 °C was added dropwise a solution of tetrabutylammonium hydroxide (0.4 mol dm⁻³; 50 cm³, 20 mmol) over ca. 15 min. The mixture was stirred for a further 2 h at 0 °C and then slightly acidified with hydrogen chloride in methanol. The mixture was allowed to stand overnight at room temperature, after which it was filtered and the residue was washed with dry methanol, and air-dried at the filter. The residue, polymer **17** (\approx 2.59 g), was dissolved in dichloromethane (100 cm³). This material had IR and ¹H NMR spectra identical with those from the material formed in method 1.

Acid and Thermal Conversion of Polymer 17 into Polymer 15.—Thin films of polymer **17** were heated at 200 °C for 12 h under a hydrogen chloride–argon flow to form polymer **15**; $\nu_{\text{max}}/\text{cm}^{-1}$ 3058, 2997, 2939, 2833, 1505, 1465, 1409, 1355, 1258, 1206, 1183, 1044, 967, 853 and 683; $\lambda_{\text{max}}/\text{nm}$ 457, 338, 258sh and 208; band-edge energy 2.34 eV. This should be contrasted with the usual value of 2.1 eV which is conventionally accepted for polymer **15** (see introduction to Experimental section).

Conclusions

We have described the base-induced polymerisation of bis-sulfonium salt monomers to afford the polyelectrolytes **3** and **9** which can be converted directly into either **4** or **10**. Conditions for fully substituting the sulfonium precursor polymers with methanol to generate the corresponding methoxy precursor polymers **5**, **11** and **17** have been optimised. The polymers obtained after heat and acid treatment have been characterised and compared with those obtained before. An important observation consisted of the fact that the sulfonium precursor polymer **8** reacted in part with methanol. This was clearly underpinned by comparison of their ¹H NMR spectra, as well as IR and UV–VIS data of the precursor polymers and the materials obtained after conversion to the poly(arylene-vinylene)s.

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