Thermal routes to low HOMO–LUMO energy gap poly(arylenevinylene)s

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We have prepared poly(2,5-dimethoxy-1,4-phenylenevinylene) (DMEOPPV) and poly(2,5-thienylenevinylene) (PTV) *via* xanthate precursor polymer routes. The respective precursor polymers can be thermally converted to their corresponding conjugated polymers without the need for acid catalysis. For both DMEOPPV and PTV the UV-visible absorption and infrared spectra were similar to the polymers when prepared *via* alkoxy precursors. Films of DMEOPPV and blends of DMEOPPV and PPV were found to be luminescent with energy being transferred from the PPV host to the DMEOPPV guest. Films of PTV or PTV–PPV blends were found not to be luminescent.

The earliest studies on the syntheses of poly(arylenevinylene)s concentrated on their formation *via* precursor polymers.[1] The precursor polymers were soluble with the solubility being at least in part due to the saturated ethylene link and the leaving group. After processing, the precursor polymer was then converted into the conjugated polymer by elimination of the leaving group generally rendering it insoluble in the solid state. Subsequent to the early work soluble poly(arylenevinylene) derivatives have been synthesised whereby the solubility is imparted by the attachment of long lipophilic groups.[2] There have been a number of leaving groups developed for the production of precursor polymers to poly(arylenevinylene)s including sulfonium,[1,3] alkoxy,[3] halo,[4] sulfinyl,[5] and xanthate[6] with the order being approximately chronological in development. However, not all leaving groups are compatible with the arylene unit. For example, whilst the sulfonium precursor can be used for the preparation of poly(1,4-phenylenevinylene) (PPV) it cannot be used with more lipophilic side group derivatives due to solvent incompatibility. In addition, with some of the more reactive arylene units such as poly(2,5-dimethoxy-1,4-phenylenevinylene) (DMEOPPV)[3,7] and poly(2,5-thienylenevinylene) (PTV)[8] the sulfonium precursor cannot easily be isolated because the sulfonium group is substituted by the nucleophilic solvents in which they are soluble. Likewise, not all leaving groups are compatible with arylene units. For example, the chloro leaving group has poor solubilising ability and hence the arylene units are required to contain solubilising groups. DMEOPPV and PTV are interesting low HOMO–LUMO energy gap poly(arylenevinylene)s. Due to their low absorption energy they are of interest for photovoltaic applications and in the case of DMEOPPV, light-emitting diodes (LEDs). The main method for the preparation of DMEOPPV and PTV involves the use of alkoxy leaving group precursor polymers that require acid catalysis for the conversion process and hence these two polymers have not been suitable candidates for device applications.[3,7,8] The acid catalysis is incompatible with device fabrication. We have recently reported that xanthate leaving groups do not react appreciably with indium–tin oxide, a commonly used electrode material, and hence xanthate groups are ideally suited for device applications.[9] In this paper we describe the first use of xanthate precursor polymers for the preparation of low HOMO–LUMO energy gap poly(arylenevinylene)s, namely DMEOPPV and PTV. We compare the physical and electronic properties of the polymers

produced by the thermal (xanthate) only route with the same polymers produced from the acid–thermal (alkoxy) conversion procedure.

Results and discussion

Monomer syntheses: The syntheses of DMEOPPV and PTV are shown in Scheme 1. In each case the xanthate monomer used was the *O*-ethyl derivative. For DMEOPPV the bis-xanthate monomer **2** was prepared from **1**[10] by treatment at room temperature with potassium *O*-ethyl xanthate in tetrahydrofuran, in the presence of a phase transfer catalyst. Under these
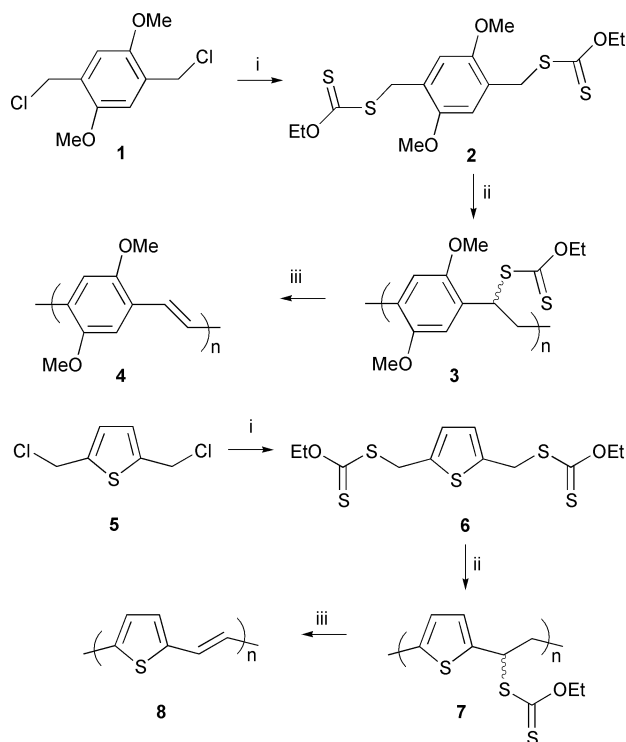
Scheme 1 *Reagents and conditions*: i, potassium *O*-ethyl xanthate, *n*-Bu$_4$NBr, DCM or THF, Ar, room temp.; ii, KOBu^t, THF, Ar; iii, heat, vacuum.

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conditions monomer **2** was isolated in a 93% yield. The bis-xanthate monomer **6** for PTV was prepared in a 63% yield from the 2,5-bis(chloromethyl)thiophene **5**[11] under similar conditions except that dichloromethane was used as the solvent.

DMEOPPV: Monomer **2** was polymerised as a 0.2 M tetrahydrofuran solution by treatment with 0.9 equivalents of a 0.4 M tetrahydrofuran solution of potassium *tert*-butoxide. The reaction was stirred at room temperature for 2.5 hours before being purified by precipitation from a tetrahydrofuran–methanol mixture. Under these conditions the precursor polymer **3** was isolated in a 32% yield. The molecular weight of a dilute solution of **3** was determined by gel-permeation chromatography (GPC) (against polystyrene standards). **3** was found to have an $\bar{M}_w$ of 2.1×10^5 and polydispersity of 6.4. Infrared analysis of **3** (Fig. 1) showed three absorptions at 1045, 1111 and 1215 cm^{-1} which we attribute, at least in part, to the xanthate leaving group. The absorptions at 1045 and 1215 cm^{-1} are broad and this is similar to that observed in other xanthate precursor polymers.[6b,c] Interestingly, the ^{1}H NMR spectrum (Fig. 2) of **3** was very different from that reported for the methoxy precursor to DMEOPPV.[3] Apart from the obvious differences associated with the different leaving groups there were also changes in the absorptions due to the aromatic and more noticably the ArOMe protons. With DMEOPPV prepared *via* the methoxy precursor there are two distinct regions for the aromatic protons whereas for the xanthate precursor these regions have coalesced. More dramatic however, are the absorptions due to the ArOMe
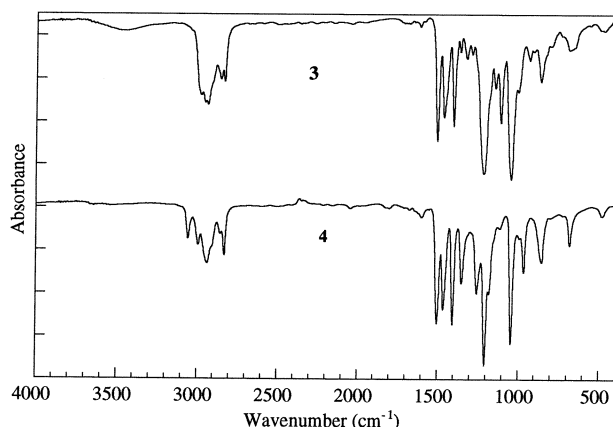

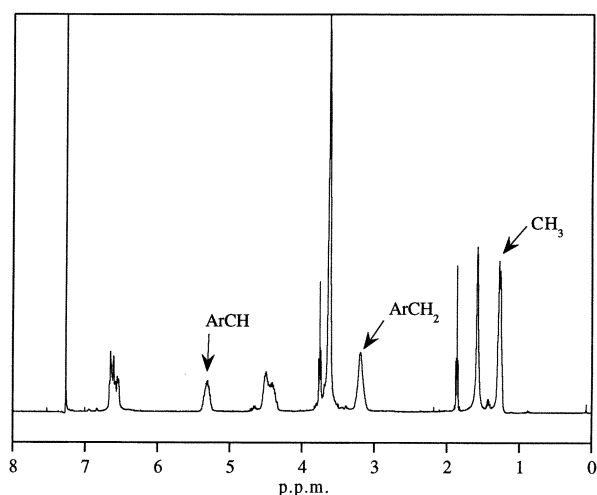**Fig. 1** Infrared spectra of films of **3** and **4**.

Fig. 2 ^{1}H NMR spectrum of **3**. The peaks at 1.59 ppm (H$_2$O), 1.86 and 3.76 (tetrahydrofuran), and 7.27 ppm (CHCl$_3$) are due to residual solvents.

protons where for the methoxy precursor there are four signals associated with the protons whereas for the xanthate precursor there was only one absorption. This clearly indicates that there are distinct structural and/or morphological differences between the two precursor polymers. The ^{1}H NMR clearly indicates that there are few conjugated units in the precursor. It has been recently reported that when using the bis-chloro monomers to form dialkoxy-PPVs that there is usually a proportion of head-to-head and tail-to-tail couplings within the polymer backbone.[12,13] The ethylene units in the dialkoxy-PPVs prepared *via* the bis-chloro monomers are observed at around 2.9 ppm in the ^{1}H NMR. In the ^{1}H NMR of precursor **3** we do not observe a significant absorbance at this chemical shift suggesting that the xanthate precursor gives good control over the regioselectivity of the polymerisation. We believe this is due to the bulk of the xanthate group relative to the chlorine atom, which would inhibit a head-to-head or 1,2-dixanthyl-ethylene arrangement. If the head-to-head arrangement is inhibited then it is only possible to have one ethylene defect in a chain. Therefore, for **3** an $\bar{M}_n$ of 3.2×10^4 and a mass per "unit" of 284 gives the number of units in the polymer of ≈ 112 which then implies that an ethylene unit, if present, would comprise less than 1% of the polymer chain. Given that it has been postulated that the non-vinylene linkage defects in PPV chains decrease the stability of LEDs based on the polymers this suggests that xanthate precursors may be a good route to overcoming the defects.[14] The importance of control over polymer structure and morphology has been clearly demonstrated for devices such as light-emitting diodes (LEDs). Thermogravimetric analysis (TGA) of **3** was initially carried out with a heating rate of 10 °C min^{-1} under nitrogen and we assign the first weight loss observed by TGA to the elimination of the leaving group. For **3**, the xanthate group was found to eliminate at 238 °C. The first weight loss occurred at 221 °C and the loss observed for **3** at this temperature was 28% which is below the 43% expected. Such a difference can be due to the precursor containing conjugated units, slow and incomplete elimination, or elimination by-products being trapped in the solid. The ^{1}H NMR showed that there was essentially no conjugation in the precursor polymer. To check whether the low weight loss was due to a slow elimination process we also carried out the TGA at 2 °C min^{-1}. Under these conditions the onset to elimination was at 207 °C with an elimination temperature of 217 °C and a weight loss of 26% was observed. This therefore suggests that either the elimination has not gone to completion or under nitrogen the by-products were trapped in the solid sample. Nevertheless, **3** was converted to **4** by heating films of **3** at 245 °C for 17 h under a dynamic vacuum and the conversion followed by both infrared (Fig. 1) and UV-visible spectroscopy (Fig. 3). The main changes observed in the infrared spectrum in going from **3** to **4** are the new
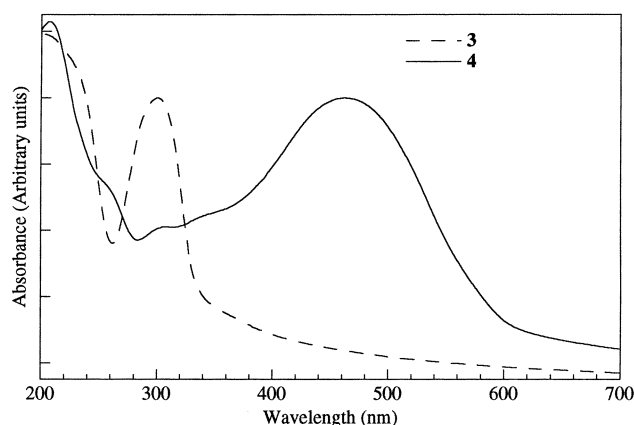

Fig. 3 UV-VIS absorption spectra of films of **3** and **4**.

absorptions at 3056 and 965 cm^{-1} which correspond to the vinyl C–H stretch and the *trans*-vinylene CH out-of-plane bend respectively.[3] In addition, the broad absorptions at 1045 and 1215 cm^{-1} in **3** become much sharper than **4** and the absorption at 1111 cm^{-1} of **3** is absent in **4** suggesting that the xanthate group has eliminated. Indeed the infrared spectrum of **4** prepared *via* the xanthate precursor polymer was identical to when **4** was prepared *via* the methoxy precursor[3] suggesting that the combination of heat and vacuum was driving the elimination reaction to completion. If there was still 35% of the xanthate leaving groups present in the polymer then absorptions due to these would be seen in the infrared spectrum. The UV-visible spectrum of PPV derivatives generally consists of two components; a UV absorption which corresponds to localised π–π* transitions and an absorption in the visible region which is due to delocalised π–π* transitions. In addition, the ratio of absorption intensity of UV to the visible components can often give an indication of the level of conjugation in the converted polymer with the smaller the ratio the better the conjugation. The precursor polymer **3** had a UV-visible absorption maximum at 300 nm which we attribute to a small number of stilbene units in the precursor polymer. After conversion to **4** there were two absorption peaks at 207 nm and one at 462 nm which correspond to the localised and delocalised transitions respectively. The absorption spectrum has no vibrational (phonon) structure on the absorption-edge which is indicative of poor intramolecular order. A similar lack of vibrational structure is observed when **4** is formed from the methoxy precursor.[7b] The onset to the absorption was ≈2.1 eV and the absorption maxima are the same as those reported in the literature.[3,7b] From these results we can conclude that the chemical and electronic structures of **4** formed by thermal treatment of the xanthate precursor are the same as those of **4** prepared from the acid–thermal treatment of the methoxy precursor. However, at this stage we cannot say whether the two materials have the same morphology.

PTV: The polymerisation of monomer **6** proved more sensitive to the conditions used and it was necessary to ensure that the conditions were strictly anhydrous. Monomer **6** was polymerised as a 1 M tetrahydrofuran solution with 0.9 equivalents of a 0.4 M tetrahydrofuran solution of potassium *tert*-butoxide. The reaction was stirred at room temperature for 1.5 hours before being purified by precipitation from a tetrahydrofuran–propan-2-ol mixture. Under these conditions the precursor polymer **7** was isolated in a 16% yield. The molecular weight of a dilute solution of **7** was determined by GPC and **7** was found to have an $\bar{M}_w$ of 7.8 × 10^4 and polydispersity of 4.5. Infrared analysis of **7** showed three absorptions at 1045, 1110, and 1218 cm^{-1} which we consider to be due, at least in part, to the xanthate leaving groups (Fig. 4). The ^{1}H NMR spectrum (Fig. 5) is consistent with the structure and indicates that little elimination has occurred during the
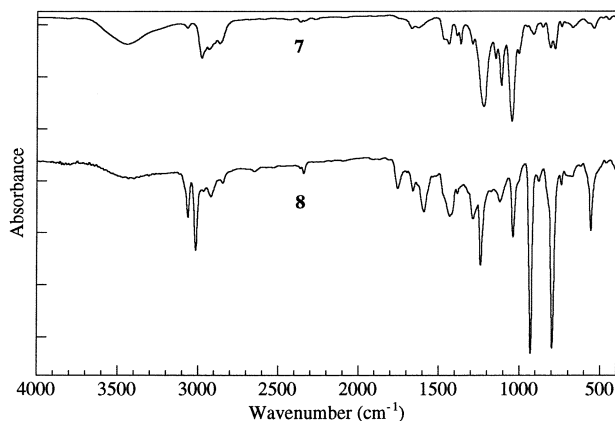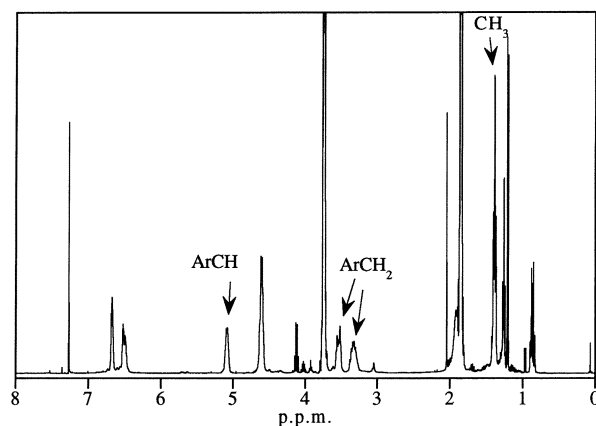

Fig. 5 ^{1}H NMR spectrum of **7**. The peaks at 1.20 ppm (propan-2-ol), 1.86 and 3.76 (tetrahydrofuran), and 7.27 ppm (CHCl$_3$) are due to residual solvents.

polymerisation and purification. An interesting feature of the ^{1}H NMR spectrum is the diastereotopic "benzylic" protons. This is similar to that observed for the precursors to PPV[3] but are absent in the ^{1}H NMR spectra of **3**. It is also interesting to note that the ^{1}H NMR spectrum of the methoxy/hydroxy precursor polymer to PTV does not show any splitting of the diastereotopic protons suggesting that apart from the obvious differences in leaving group there is also a difference in the structure/morphology of the different precursor polymers.[8a] TGA of **7** was carried out with a heating rate of 10 °C min^{-1} under nitrogen and we again assign the first major weight loss observed by TGA to the elimination of the leaving group. For **7**, the xanthate group was found to eliminate at 219 °C. The onset to weight loss occurred at 202 °C and the loss observed for **7** was 34% which was below the expected 53%. Decreasing the heating rate to 2 °C min^{-1} gave an elimination temperature of 191 °C and weight loss of 31%. As in the case of DMEOPPV we believe that this is due to either elimination by-products being trapped in the solid sample or incomplete elimination under the experimental conditions. The conversion of **7** to **8** was followed by infrared (Fig. 4) and UV-visible spectroscopy (Fig. 6). Films of **7** were heated at 220 °C for 21 hours under dynamic vacuum to form **8**. On conversion the infrared spectrum of **8** showed that the three absorptions at 1045, 1110, and 1218 cm^{-1} are absent indicating that the xanthate group has left and the conversion gone to completion. In their place are absorptions at 3062, 3014 and 929 cm^{-1} with the first two corresponding to C–H stretches and the latter to the *trans*-vinylene CH out-of-plane bend.[8b] The infrared spectrum of **8** prepared from **7** was identical to that reported in the literature for PTV prepared from the methoxy precursor indicating that they have the same chemical structure.[7b] The UV-visible

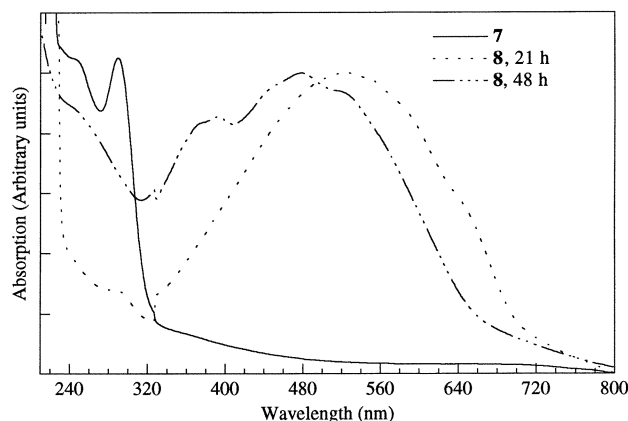**Fig. 4** Infrared spectra of films of **7** and **8**.

Fig. 6 UV-VIS absorption spectra of films of **7** and **8**.

spectra of **7** and **8** are shown in Fig. 6 and it can be clearly seen that on conversion there is a new absorption at longer wavelength which is due to delocalised π–π* transitions. The onset to absorption is ≈700 nm (≈1.8 eV) and the absorption maxima is at 524 nm (2.4 eV). These are both blue shifted by about 20 nm when compared with PTV prepared *via* the acid–thermal treatment of the methoxy/hydroxy precursor.[7b] However, the band edge does have phonon structure indicating a degree of intramolecular order. Interestingly, when the conversion time was extended to 48 hours there was a blue shift in the absorption which itself had increased phonon structure.

Blends: Neat films of DMEOPPV have been reported to be weakly fluorescent in the solid state whilst we are not aware of any reports of PTV being fluorescent.[14] In the case of DMEOPPV, dialkoxy-PPV derivatives that contain at least one longer chain such as MEHPPV are fluorescent and have been successfully used as orange–red emitters in LEDs. However, the disadvantage of these longer chain polymers is that the lipophilic side chain acts as an electrical insulator. Now that we had a route to DMEOPPV that was compatible with device preparation we were interested to see whether the neat material was fluorescent. In addition, we studied whether the DMEOPPV could be formed in a blend with a host polymer in order to separate the chains and achieve energy transfer from the host polymer to the guest DMEOPPV. As the ultimate goal with precursor routes is to form insoluble films of the conjugated polymer, the polymer chosen as the host was PPV which itself can be prepared *via* the xanthate precursor polymer **9**.[6a] Films of PPV, 5% DMEOPPV in PPV, 25% DMEOPPV in PPV, and neat DMEOPPV were prepared. The films of PPV and DMEOPPV were formed from their respective xanthate precursors at 220 °C for 17 and 15 hours respectively under vacuum. The blends of conjugated polymers were prepared by mixing the required ratios of precursor polymers by weight, spin-coating to form thin films, followed by thermal conversion at 240 °C for 17 hours. The blended DMEOPPV–PPV films were of good quality and there was no phase separation observable to the eye. We found that the presence of the two polymers in the same film did not inhibit the individual conversion processes. Infrared analysis of the films showed the absence of the absorptions due to the xanthate leaving groups. In their place the absorptions due to the conjugated polymers were found. The absorption and photoluminescence (PL) spectra of the films are shown in Fig. 7. The neat DMEOPPV film was fluorescent with maxima at 595 nm (2.08 eV), 630 nm (1.97 eV), and a shoulder at 648 nm (1.91 eV) and which is
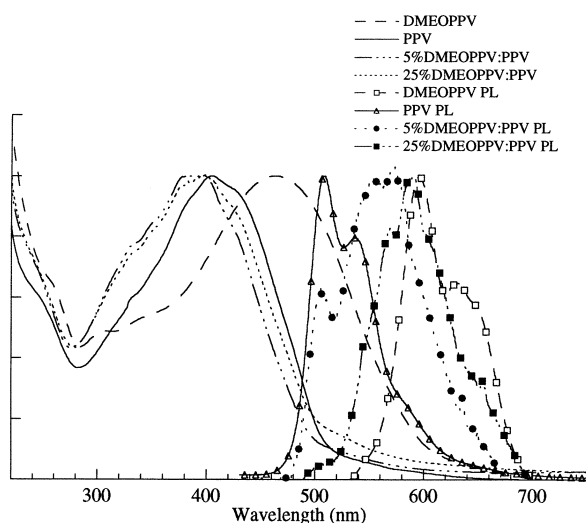
similar to that reported for DMEOPPV formed from the methoxy precursor polymer. The Commission Internationale d'Eclairage 1931 (C.I.E.) co-ordinates for DMEOPPV were determined to be (0.55, 0.44) which corresponds to an orange–red emission. The PL spectrum of the PPV had peaks at 507 nm (2.45 eV) and 536 nm (2.31 eV) and a shoulder at 581 nm (2.13 eV) which are at the same positions as PPV prepared from the sulfonium precursor polymer. The UV-visible spectrum of the blends show a slight blue shift in the main absorption peak when compared to the absorption of PPV. However, in the 25% blend there is a slight increase in the absorption at longer wavelength which should correspond to the DMEOPPV. Indeed in a 50:50 blend the absorption of the DMEOPPV is clearly visible. The blend films were excited at the absorption maxima. The PL spectrum of the 5% DMEOPPV–PPV blend shows emission from both the PPV host and the DMEOPPV whilst the 25% blend shows emission predominantly from the DMEOPPV. This indicates that energy is being transferred from the PPV host to the DMEOPPV guest for emission. This suggests that blends of PPV–DMEOPPV might be useful for electroluminescence applications. In contrast, the neat films of PTV were as expected not fluorescent. In addition the 5% and 25% blends of PTV in PPV also showed no emission. Given that PPV itself is luminescent this suggests that the energy was transferred from the host PPV to the PTV where it is quenched. The UV-visible spectra (Fig. 8) of the PTV–PPV blends show an increasing absorption at 540 nm in line with increasing PTV content. Again the infrared spectra showed that the elimination had gone to completion in the PPV–PTV blends.

In conclusion, we have demonstrated that the xanthate precursor route can be used for the preparation of low HOMO–LUMO energy gap poly(arylenevinylene)s, namely DMEOPPV and PTV. The xanthate precursors clearly have structural and/or morphological differences to the alkoxy precursors to the same polymers. However, on thermal conversion the chemical structures and optical properties of the polymers formed from the xanthate precursors were found to be similar to the same polymers produced *via* an acid–thermal conversion process. These results open up the possibility of using insoluble low HOMO–LUMO energy gap poly(arylenevinylene)s in devices.

Experimental

Measurements

NMR spectra were recorded on a Bruker DPX400 MHz spectrometer. ^{13}C NMR spectra were fully decoupled. IR spectra were recorded on a Perkin–Elmer Paragon 1000 Infrared spectrometer. UV-visible spectra were recorded on Perkin–Elmer UV-Visible (Lambda 14P) spectrophotometer, and unless otherwise stated all spectra were recorded as a

Fig. 7 UV-VIS absorption and photoluminescence spectra of films of PPV, DMEOPPV and blends of the two polymers.
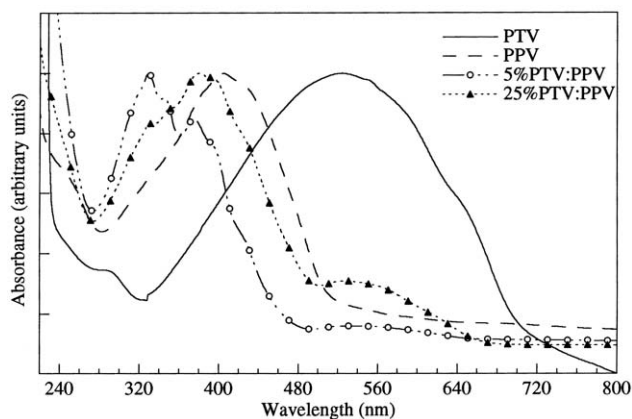
Fig. 8 UV-VIS absorption spectra of films of PPV, PTV and blends of the two polymers.

solution in dichloromethane. Mass spectra were recorded on a VG Autospec spectrometer, the mode of ionisation being stated in each case. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were carried out by the Inorganic Chemistry Laboratory, Oxford or Elemental Microanalysis Ltd, UK. Gel permeation chromatography was carried out using PLgel 20 μm Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($\bar{M}_p = 580 - 11.6 \times 10^6$) in tetrahydrofuran with toluene as flow marker at $30 \pm 0.1\,^\circ C$. The samples for GPC were filtered through a teflon membrane (0.45 μm). The tetrahydrofuran was degassed with helium and pumped at a rate of $1\,cm^3\,min^{-1}$. The PL spectra of thin films were measured using a Instruments S.A. Inc., Fluoro Max-2 fluorimeter with excitation at the absorption maximum. Films were prepared for the PL measurements by spin-coating the precursor polymers from tetrahydrofuran at 2000 rpm for 1 minute, followed by thermal conversion under dynamic vacuum. The following conditions were used in each case: DMEOPPV ($40\,mg\,cm^{-3}$ of **3**; $220\,^\circ C$, 15 h); DMEOPPV–PPV blends ($40\,mg\,cm^{-3}$ of **3** plus **9**; $240\,^\circ C$, 17 h); PTV–PPV blends ($30\,mg\,cm^{-3}$ of **3** plus **9**; $220\,^\circ C$, 15 h); PPV ($10\,mg\,cm^{-3}$ of **9**; $220\,^\circ C$, 17 h). The thermogravimetric analysis was carried out on a Perkin–Elmer Thermogravimetric Analyser, TGA 7. For each run the sample was held either at $25\,^\circ C$ for 15 min and then heated from 25–$600\,^\circ C$ at $10\,^\circ C\,min^{-1}$ or $25\,^\circ C$ for 10 min and then heated from 25–$600\,^\circ C$ at $2\,^\circ C\,min^{-1}$ with analysis in both cases carried out under nitrogen.

1,4-Bis[ethoxy(thiocarbonyl)thiomethyl]-2,5-dimethoxybenzene 2

A solution of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene **1**[10] (1.0 g, 4.9 mmol), potassium O-ethyl xanthate (1.97 g, 12.3 mmol), and tetra-n-butylammonium bromide (0.32 g, 0.98 mmol) in dry tetrahydrofuran ($20\,cm^3$) was stirred under Ar at room temperature overnight. The solution was passed through a plug of silica using dichloromethane as eluent to give **2** (1.71 g, 93%) as a white solid, mp $128\,^\circ C$. (Found: C, 47.16; H, 5.44%. $C_{16}H_{22}O_4S_4$ requires C, 47.26; H, 5.45%); ν_{max} (KBr)/cm^{-1} 1037, 1050, and 1215; λ_{max} (CH$_2$Cl$_2$)/nm 285 (log ε/dm^3 mol^{-1} cm^{-1} 4.38); δ_H (400 MHz; CDCl$_3$) 1.43 (6 H, t, J 7.0, 2 × OCH$_2$CH$_3$), 3.81 (6 H, s, 2 × OCH$_3$), 4.37 (4 H, s, 2 × ArCH$_2$S), 4.66 (4 H, q, J 7.0, 2 × OCH$_2$CH$_3$) and 6.93 (2 H, s, ArH); δ_C (100 MHz; CDCl$_3$) 13.8, 35.3, 56.1, 69.9, 113.4, 124.3, 151.1 and 214.9; m/z [EI+] 406 (M$^+$, 5%), 285 {M$^+$ − 121 [SC(S)OEt], 100}.

Poly{2,5-dimethoxy-1,4-phenylene[1-ethoxy(thiocarbonyl)-thio]ethylene} 3

A solution of potassium tert-butoxide (0.174 g, 1.55 mmol) in dry tetrahydrofuran ($3.9\,cm^3$) was added to a solution of **2** (0.70 g, 1.7 mmol) in dry tetrahydrofuran ($8.6\,cm^3$) under Ar. The reaction mixture was stirred at room temperature for 2.5 h before being poured onto methanol ($45\,cm^3$) with dry terahydrofuran washings ($3\,cm^3$). The mixture was centrifuged (4500 rpm, 10 min) and the supernatant removed. The residue was dissolved in dry tetrahydrofuran ($3\,cm^3$) and then added to methanol ($21\,cm^3$). The mixture was centrifuged (4500 rpm, 10 min), the supernatant removed, and the yellow precipitate of **3** (158 mg, 32%) was dissolved in dry tetrahydrofuran ($2\,cm^3$); ν_{max} (film)/cm^{-1} 1045 and 1215 (SC=S); λ_{max} (film)/nm 300; δ_H (400 MHz; CDCl$_3$) 1.21–1.34 (3H, br m, CH$_3$), 3.11–3.27 (2H, br m, CH$_2$), 3.51–3.72 (6H, br s, OCH$_3$), 4.33–4.56 (2H, br m, OCH$_2$), 5.24–5.39 (1H, br m, CH), and 6.53–6.69 (2H, br m, ArH); GPC ($1\,mg\,cm^{-3}$) $\bar{M}_n = 3.2 \times 10^4$, $\bar{M}_w = 2.1 \times 10^5$, polydispersity index = 6.4; thermogravimetric analysis: $238\,^\circ C$ (weight loss: 28%; expected: 43%).

Poly(2,5-dimethoxy-1,4-phenylenevinylene) 4

Thin films of **3** were heated at $245\,^\circ C$ under a dynamic vacuum for 17 h to give **4**; ν_{max} (film)/cm^{-1} 965 and 3056 (CH=CH); λ_{max} (film)/nm 207 and 462.

2,5-Bis[ethoxy(thiocarbonyl)thiomethyl]thiophene 6

A solution of 2,5-bis(chloromethyl)thiophene **5**[11] (0.94 g, 5.2 mmol), potassium O-ethyl xanthate (2.09 g, 13.0 mmol), and tetra-n-butylammonium bromide (0.50 g, 1.6 mmol) in dry dichloromethane ($30\,cm^3$) was stirred under Ar at room temperature for 20 hours. The solution was filtered and concentrated in vacuo. The concentrated solution containing the crude product was purified by passage through a plug of silica using dichloromethane as eluent to give **6** (1.16 g, 63%) as a colourless oil which solidified to a white solid, mp 36–$37\,^\circ C$. (Found: C, 40.87; H, 4.53%. $C_{12}H_{16}O_2S_5$ requires C, 40.88; H, 4.57%); ν_{max} (KBr)/cm^{-1} 1048, 1111, and 1217; λ_{max} (CH$_2$Cl$_2$)/nm 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.12) and 284 (4.39); δ_H (400 MHz; CDCl$_3$) 1.44 (6 H, t, J 7.0, 2 × OCH$_2$CH$_3$), 4.51 (4 H, s, 2 × SCH$_2$), 4.67 (4 H, q, J 7.0, 2 × OCH$_2$CH$_3$) and 6.83 (2 H, s, ArH); δ_C (100 MHz; CDCl$_3$) 13.8, 35.0, 70.3, 126.8, 138.6 and 213.1; m/z [CI+] 231 {M$^+$ − 121 [SC(S)OEt], 100%}.

Poly{2,5-thienylene[1-ethoxy(thiocarbonyl)thio]ethylene} 7

A solution of potassium tert-butoxide (0.20 g, 1.79 mmol) in dry tetrahydrofuran ($4.6\,cm^3$) was added to a solution of **6** (0.70 g, 2.00 mmol) in dry tetrahydrofuran ($2.0\,cm^3$) under Ar. The reaction mixture was stirred at room temperature for 1.5 h before being poured onto ice-cold propan-2-ol ($15\,cm^3$) with dry tetrahydrofuran washings ($2\,cm^3$). The mixture was centrifuged (4500 rpm, 10 min), the supernatant removed, and the residue dissolved in dry tetrahydrofuran ($3\,cm^3$). The solution was poured onto ice-cold propan-2-ol ($10\,cm^3$) and the mixture centrifuged (4500 rpm, 10 min). The supernatant was removed and the yellow precipitate of **7** (75 mg, 16%) dissolved in dry tetrahydrofuran ($3\,cm^3$); ν_{max} (film)/cm^{-1} 1045, 1110, and 1218; λ_{max} (film)/nm 289; δ_H (400 MHz; CDCl$_3$) 1.35–1.43 (3H, br t, CH$_3$), 3.25–3.40 (1H, br m, CH$_2$), 3.48–3.59 (1H, br m, CH$_2$), 4.56–4.67 (2H, br m, OCH$_2$), 5.04–5.13 (1H, br m, CH), 6.45–6.55 (1H, br m, ArH) and 6.64–6.71 (1H, br m, ArH); GPC ($1\,mg\,cm^{-3}$) $\bar{M}_n = 1.7 \times 10^4$, $\bar{M}_w = 7.8 \times 10^4$, polydispersity index = 4.5; thermogravimetric analysis: $219\,^\circ C$ (weight loss: 34%; expected: 53%).

Poly(2,5-thienylenevinylene) 8

Thin films of **7** were heated at $220\,^\circ C$ under a dynamic vacuum for 21 h to give **8**; ν_{max} (film)/cm^{-1} 929, 3014, and 3062; λ_{max} (film)/nm 218 and 524.

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