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Comparison of the electronic properties of poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] prepared by different precursor polymer routes

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The synthesis of poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] **10** *via* chloro **7**, *S*-methyl xanthate **8**, and *O*-ethyl xanthate **9** precursor polymers has been investigated. We found that the chloro and *O*-ethyl xanthate precursor polymers could be easily formed whilst the *S*-methyl xanthate gave only low molecular weight material. The observed molecular weights of the chloro and *O*-ethyl xanthate precursor polymers were found to decrease with decreased polymer concentration when measured by gel permeation chromatography (GPC) with the decrease probably being due to the dissociation of polymer aggregates or physical networks. In contrast, no decrease of molecular weight was observed by GPC for the *S*-methyl xanthate precursor polymer on dilution. The chloro, *S*-methyl xanthate, and *O*-ethyl xanthate precursor polymers were thermally converted to the conjugated polymer **10**. The UV–visible absorption and photoluminescence quantum yield of **10** was determined to be strongly dependent on the precursor route used. For **10** formed from the chloro precursor **7** the PL quantum yield was found to be 55 ± 5%.

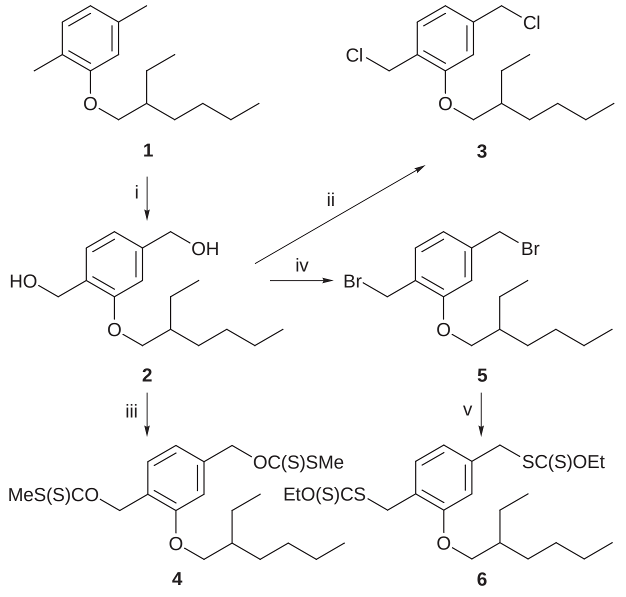
There has been an increased interest in poly(1,4-phenylenevinylene) (PPV) and its derivatives since it was first shown that PPV could act as the light-emitting layer in a light-emitting diode (LED).[1] Much effort has gone into determining the effect of substituents on the electronic properties of and the synthetic pathways to PPV and its derivatives. The two main synthetic routes to PPV have involved the synthesis of soluble conjugated derivatives, which are normally substituted with long lipophilic groups, or *via* a precursor polymer route which generally leads to insoluble polymers.[2] Of the two main synthetic routes, we have concentrated on the latter as it gives rise to materials which can be easily incorporated into multilayer LEDs.[3] There are now a number of precursor routes to PPV and its derivatives including, sulfonium,[4] alkoxy,[4b] halo,[5,3c] xanthate (dithiocarbonate),[6] and sulfoxide and sulfone.[7] It is clear that different precursor routes to the same conjugated polymer can give rise to polymers which have similar chemical structures but different electronic properties. Of particular interest to us was the report that the xanthate precursor to PPV gives higher external quantum efficiencies when used as the light-emitting layer in an LED than PPV prepared from the traditional sulfonium route.[6] This was attributed to the introduction of *cis* linkages which made the material amorphous and have shorter conjugation lengths. However, it was not made clear whether the PPV produced *via* the *O*-ethyl xanthate route was itself inherently more luminescent. We were therefore interested in exploring the effect of the xanthate leaving group on the photoluminescence quantum yield of a 2-alkoxyPPV derivative.

2-AlkoxyPPVs have been prepared *via* sulfonium precursor polymers[8] and even directly providing the alkoxy side chain was a long lipophilic group.[9] Our interest in 2-alkoxyPPVs arises because we have used a 2-(2′-ethylhexyloxyphenyl) group as the basic 'carrier' monomer for PPV derivatives which contain electron-withdrawing groups.[5a,d] We were therefore interested in how the precursor route used could affect the photophysical properties of the basic unsubstituted polymer. In this paper we describe the synthesis of a new 2-alkoxyPPV, poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] **10** (EHPPV) *via* chloro **7** and *O*-ethyl xanthate **9** polymers, and a new *S*-methyl xanthate **8** precursor polymer. We compare the syntheses and properties of the precursor polymers and the electronic properties of the EHPPV produced by the different routes.

Results and discussion

Monomer syntheses

The strategy for the syntheses of the monomers for EHPPV is shown in Scheme 1. The first step in the synthesis of all three monomers investigated was the activation of the two methyl groups of **1**.[5a] This was achieved by free radical bromination using *N*-bromosuccinimide in carbon tetrachloride heated at reflux. Under these conditions an inseparable mixture of brominated products was formed. To facilitate



Scheme 1 *Reagents and conditions:* i, NBS, CCl_4, AIBN, Δ, then NaOAc, CH_3COOH, Δ, then KOH, H_2O, MeOH, DCM, Δ; ii, DMAP, tosyl chloride, triethylamine, DCM, room temp., Ar; iii, NaH, THF, room temp., then CS_2, room temp., then MeI, room temp., Ar; iv, PBr_3, DCM, room temp., Ar; v, potassium *O*-ethyl xanthate, $(n\text{-Bu})_4NBr$, DCM, Ar, room temp.

the separation of the desired di-activated *p*-xylene from the mono-activated *p*-xylenes and other by-products the brominated mixture was acetylated to form the corresponding acetates using sodium acetate in glacial acetic acid heated at reflux. Unfortunately, the acetates were not separable as reported in another synthesis using this strategy[5a] and the acetates had to be hydrolysed with potassium hydroxide in aqueous methanol to give the crude benzyl alcohols. The desired benzyl alcohol **2** was then separable by chromatography from the other by-products and could be isolated in a total yield of up to 46% for the 6 reactions. The chloro monomer **3** was formed from **2** by treatment of **2** with a mixture of tosyl chloride, DMAP, and triethylamine[10] and was isolated in a 58% yield. The bis-(*S*-methyl xanthate) monomer **4** was also prepared from **2**. This was achieved by reacting the dialkoxy anion of **2** with carbon disulfide followed by quenching with methyl iodide. Under these conditions **4** was formed in a yield of 66%. Finally the bis-(*O*-ethyl xanthate) monomer **6** was prepared in 98% yield from the bromo monomer **5** by reaction with potassium *O*-ethyl xanthate in the presence of a phase transfer catalyst. The bromo monomer **5** was synthesised from **2** by treatment with phosphorus tribromide in an 84% yield.

Polymerisations and conversions

The polymerisations of all three monomers were carried out under similar conditions (Scheme 2). The general procedure involved the addition of approximately 0.9 equivalents of a solution of potassium *tert*-butoxide in tetrahydrofuran to a solution of the monomer in tetrahydrofuran. To compare the utility of each of the monomers for the preparation of the precursor polymers the polymerisations were all carried out at a concentration of 0.13–0.15 M with ice bath cooling. When these conditions were used **7**, **8**, and **9** were formed in ~57%, ~38%, and ~68% yields respectively. All three polymers had good solubility in tetrahydrofuran. The molecular weights of the precursor polymers were studied by gel permeation chromatography (GPC) against polystyrene standards. Both the chloro **7** and *O*-ethyl xanthate **9** precursor polymers had molecular weights which appeared to be concentration dependent. If the stock solutions of polymer were diluted for GPC analysis and run immediately then the chloro precursor polymer **7** had an initial $\bar{M}_w$ of about 1.6×10^6 and a polydispersity of ~4.7 and the *O*-ethyl xanthate polymer, **9**, had an $\bar{M}_w = 7.7 \times 10^5$ with a polydispersity of 2.4. The inaccuracy in the observed molecular weight of **7** arises because the high molecular weight component of **7** is above the calibration limits of the GPC column used (Fig. 1a). On equilibration at the lower concentrations used for GPC analysis the $\bar{M}_w$s of **7** and **9** were observed to decrease with a concomitant change in the polydispersities such that **7** had an $\bar{M}_w = 4.4 \times 10^5$ and a polydispersity of 1.8 (Fig. 1a) and **9** an $\bar{M}_w = 2.6 \times 10^5$ with a polydispersity of 1.7 (Fig. 1b). The decrease in $\bar{M}_w$ observed by GPC analysis for **7** and **9** on dilution and equilibration is similar to that seen for some other precursor polymers which have been used to prepare PPV derivatives and we believe this occurs due to the dissociation of polymer aggregates or physical networks.[11,5d] In contrast the *S*-methyl xanthate monomer **4** only gave very low molecular weight **8** which had an $\bar{M}_w$ of 8.5×10^3 and a polydispersity of 1.8. Attempts at increasing the molecular weight of **8** by employing higher concentrations of monomer, base, or temperature gave no improvement. For example, adding 1 M base solution to neat monomer **4** and carrying out the reaction at 55–60 °C for 1 h gave **8** in a 41% yield which had an $\bar{M}_w = 5.5 \times 10^3$ and a polydispersity of 1.7. However, ^{1}H NMR analysis of **8** produced at the higher temperature and under more concentrated conditions indicated that it contained a greater proportion of conjugation than **8** produced at lower temperatures and concentrations.

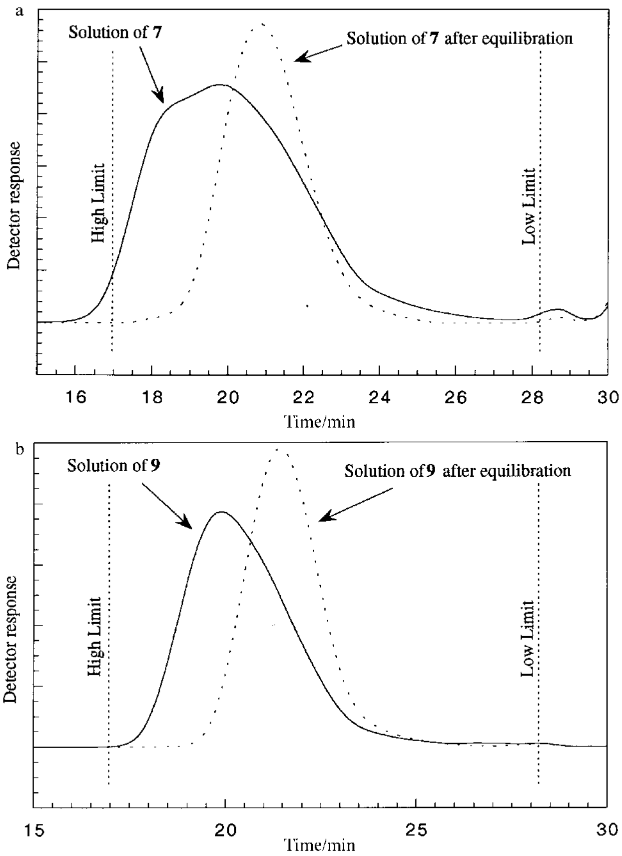
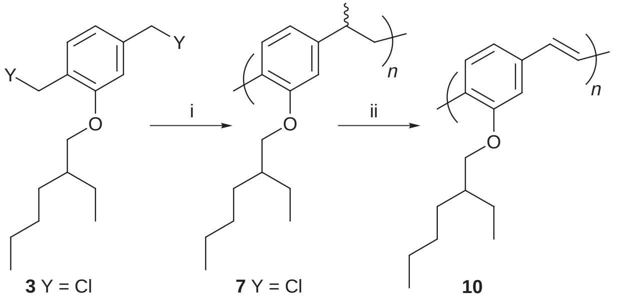


Fig. 1 a) GPC traces of **7**; b) GPC traces of **9**.

Thermogravimetric analysis (TGA) of polymers **7**, **8**, and **9** was carried out with a heating rate of 5 °C min^{-1}. In each case we expect that the first weight loss corresponds to the elimination of the leaving group. For **7**, hydrogen chloride was found to eliminate at 234 °C, with the first weight loss ocurring at ~205 °C. Similarly, TGA of **9** indicated that the *O*-ethyl xanthate group was eliminated at 236 °C with the elimination beginning at ~213 °C. For both **7** and **9** the weight loss observed corresponded closely to that expected for the elimination from a precursor polymer with only low levels of conjugation. ^{1}H NMR also indicated that there were only low levels of conjugation in **7** and **9**. The amount of conjugation in these precursor polymers can be determined approximately by comparing the integration of the benzylic methine proton with the signal due to the OCH_2 protons of the 2-ethylhexyloxy side group. In the case of **8** the elimination process was more complex. There was an initial elimination at 126 °C which commenced at ~102 °C and corresponded to a weight loss of around 12%. After this there was almost a continuous weight



3 Y = Cl
4 Y = OC(S)SMe
6 Y = SC(S)OEt

7 Y = Cl
8 Y = OC(S)SMe
9 Y = SC(S)OEt

10

Scheme 2 *Reagents and conditions:* i, KOBu^t, THF, Ar; ii, heat, vacuum.

loss until 425 °C when the polymer decomposed. The weight loss up to the decomposition point was ~41% which is above the expected mass loss (32%) of **8** on conversion to **10**. This was clearly different to the thermal properties of **7** and **9** for which the weight loss was well defined and corresponded closely to the theoretical loss of weight associated with the elimination reaction. We are unsure as to why the elimination process for **8** is so complex but it may be due to the low molecular weight of the polymer. In addition, it is important to note that the ^{1}H NMR of **8** was much more complex than the NMR spectra for **7** and **9** with a large number of signals in the methine region and signals due to the conjugated units. The complexity in the ^{1}H NMR spectrum could be due to a combination of factors including the presence of different structural isomers, different molecular weight polymers having different conformations in solution, or different levels of conjugation in the polymer chains.

In the initial report on the *O*-ethyl xanthate precursor route to PPV it was noted that the significant levels of *cis*-vinylene linkages could be formed during the elimination procedure. We were therefore interested to compare the properties of the conjugated polymer **10** that was formed from each of the three precursor polymers. All three precursor polymers were converted in the range of 209–218 °C under vacuum overnight and properties of **10** formed from the different precursor polymers were compared by UV–visible spectroscopy and infrared spectroscopy. There are usually two main features observed in the UV–visible spectrum of a conjugated polymer based on PPV; first, there is an absorption in the visible region due to delocalised π–π* transitions; and second, there is an absorption in the UV which corresponds to localised π–π* transitions. In addition, with PPV based polymers an insight into the degree of conjugation can be gained by comparing the ratio of the localised to the delocalised transitions with the smaller the ratio the better the conjugation. Thermal conversion of **7** gave **10** which had peaks at 210 nm and 450 nm (localised π–π* and delocalised π–π* absorptions respectively). As can be seen in Fig. 2 the two peaks are of similar intensity which indicates that when **10** is produced from **7** it has good conjugation. In addition, the infrared spectrum of **10** (Fig. 3) when formed from **7** shows a strong absorption at 965 cm^{-1} which is attributed to the *trans*-vinylene CH out-of-plane bend. Films of **10** formed from **7** were found to be insoluble in chloroform, tetrahydrofuran, and toluene. When **10** was formed from **9** a similar result was observed with the UV–visible absorption spectra having a peak at 445 nm. As in the case of **10** produced from **7**, the peak at 445 nm for **10** formed from **9** is of similar intensity to that at 208 nm indicating that the degree of conjugation in the two materials is essentially the same. The UV–visible spectrum of **10** produced from **9** therefore suggests that the conversion has gone basically to completion. The essentially complete conversion of **9** to **10** was confirmed by the comparison of the infrared spectra of **9** and **10** (Fig. 4). The precursor polymer **9** has strong absorptions at 1219 and 1049 cm^{-1} which are due to the *O*-ethyl xanthate leaving group and it can be clearly seen that these are absent in the sample of **10** formed from **9**. Instead in the sample of **10** we again see the stretch at 965 cm^{-1} which corresponds to the *trans*-vinylene CH out-of-plane bend. The absorption maximum of **10**, which has one alkoxy group, falls as expected between the absorption maxima for PPV (427 nm)[4b] and a dialkoxyPPV such as MEHPPV (492 nm).[3c]

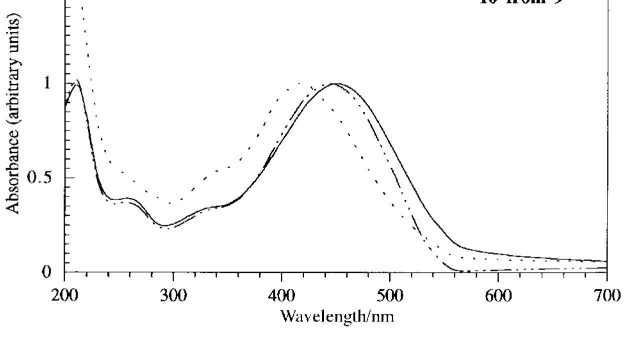


Fig. 2 UV–VIS absorption spectra of **10** formed from **7**, **8**, and **9**.

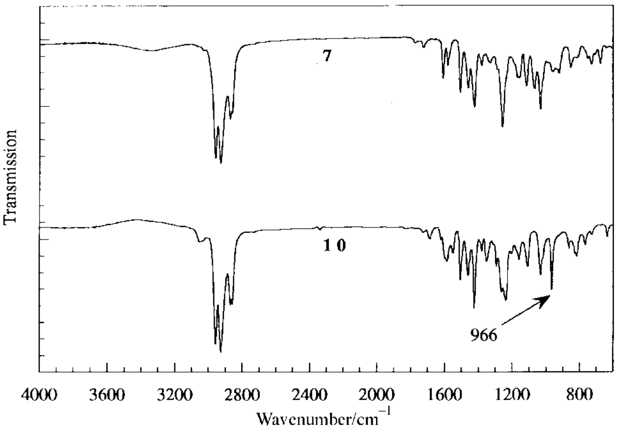


Fig. 3 Infrared spectra of **7** and **10** formed from **7**.

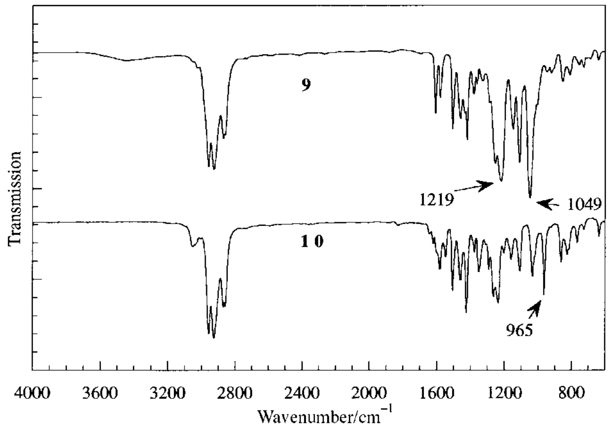


Fig. 4 Infrared spectra of **9** and **10** formed from **9**.

In contrast, when **10** is prepared from **8** the onset of absorption and peak (417 nm) are blue shifted compared to **10** prepared from **7** or **9** (Fig. 2). This could be due to a number of reasons including conformational defects, short chain length, or incomplete conversion. Determining the extent of conversion of **8** to **10** by infrared analysis is complicated. Normally we expect to observe in the conjugated polymer an absorption at around 965 cm^{-1} corresponding to the *trans*-vinylene CH out-of-plane bend. However, in both the *S*-methyl xanthate monomer **4** and precursor polymer **8** there are already absorptions in this region and in the latter case this may be due to some conjugation in the polymer. Nevertheless, for **8** there is an absorption at 1060 cm^{-1} and a broad absorption at 1217 cm^{-1} which we believe are associated with the *S*-methyl xanthate leaving group (Fig. 5). Under the conversion conditions used the absorptions due to the *S*-methyl xanthate leaving group are not observed in films of **10** and there is a concommitant increase in the stretch at 966 cm^{-1}. In addition, the infrared spectrum of **10** formed from **8** (Fig. 5) is similar to **10** formed from **7** or **9** (Fig. 3 and 4). To determine whether the blue shift in the absorption spectrum is due to short chain lengths is more difficult. GPC analysis of **8** gives an $\bar{M}_w$ of 8.5×10^3 and $\bar{M}_n$ of 4.7×10^3

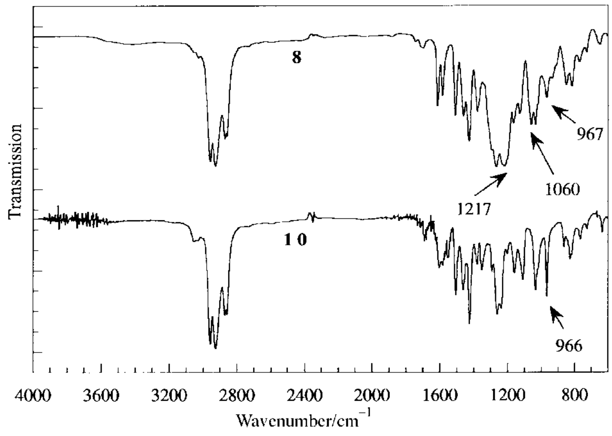


Fig. 5 Infrared spectra of **8** and **10** formed from **8**.

which would correspond to approximately 25 or 14 units respectively assuming that **8** has a similar structure to the polystyrene standards. Although this may be an over estimation of the number of units, given that the HOMO–LUMO energy gap of model compounds of PPV decrease quickly as the number of 'monomer units' increases such that after around six units are in place the HOMO–LUMO energy gap is similar to PPV[12] we would conclude that the blue shift in absorption is probably not due to excessively short chain lengths. This is strengthened by the fact that uniform thin films of **8** can be easily prepared by spin-coating. We therefore conclude that the blue shift observed in the UV–visible spectrum is probably due to conformational effects. The poorer conjugation is observed not only in the blue shift of the peaks but also in the ratios of the peaks 205 and 405 nm where the longer wavelength absorption is of lower intensity.

Given the similarities in the UV–visible absorption spectra of **10** produced from **7** and **9** it might be expected that their photoluminescence (PL) spectra and quantum efficiencies should be the same, with that of **10** formed from **8** being different. For the PL studies **7**, **8**, and **9** were converted to **10** at 220 °C at <0.001 mBar for 15.5 h. The PL spectra of **10** produced from each of the precursor polymers are illustrated in Fig. 6. The first point to note is that each of them shows good vibronic structure which indicates that the **10** produced in each case has good intramolecular order. The vibronic structure observed is similar to that reported for 2-methoxyPPV and 2-*n*-butyloxyPPV[8a] and indicates that the longer 2-ethylhexyloxy group is not adding any significant disorder to the polymer. As in the case of the UV–visible spectrum there is a blue shift in the PL of **10** produced from **8** although it is smaller than that observed in the absorption spectrum. This is consistent with the singlet excited state migrating to the regions of lowest HOMO–LUMO energy gap in the polymer which are similar to **10** produced from the other two precursor polymers. In contrast the PL quantum yield varied widely for **10** produced *via* the different precursor polymers. When **10** was produced from **7** the PL quantum yield was 55 ± 5% and when formed from **8** and **9** was 37 ± 4% and 17 ± 2% respectively. These values should be compared to the 27% observed for PPV[13] and the 10–15% observed for the dialkoxyPPV, MEHPPV.[13,3c] The PL quantum yield of 55 ± 5% is remarkably high for an alkoxy substituted PPV and is in marked contrast to the results reported for 2-methoxyPPV and 2-*n*-butyloxyPPV when they were compared to PPV.[8a] Although the absolute quantum efficiencies are not reported the relative quantum efficiencies of 2-methoxyPPV and 2-*n*-butyloxyPPV to PPV, which was taken as 1, were 0.43 and 0.48 respectively at 290 K.[8a] The difference in the PL quantum yield between **10**, and 2-methoxyPPV and 2-*n*-butyloxyPPV may be due to the longer side chain. Therefore, our results clearly show that subtle changes in the synthesis of **10** can have a strong effect on its PL quantum yield. The differences in the PL quantum yield may be due to different sample morphologies which can give rise to different inter- or intra-chain interactions.

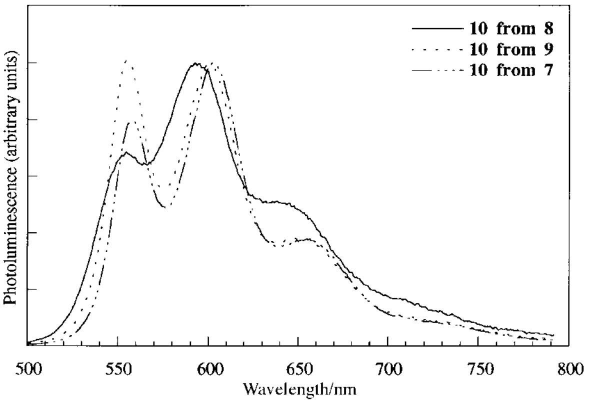


Fig. 6 Photoluminescence spectra of **10** formed from **7**, **8**, and **9**.

In conclusion, we have prepared a new 2-alkoxyPPV, EHPPV, *via* chloro, *O*-ethyl xanthate, and *S*-methyl xanthate precursor polymers. The use of an *S*-methyl xanthate precursor polymer has not been reported before for the preparation of poly(arylenevinylene)s. All three polymers could be thermally converted to give samples of EHPPV which had similar PL spectra but remarkably different PL quantum yields with the chloro precursor polymer **7** giving rise to an alkoxyPPV derivative with an exceptionally high PL quantum yield. We plan to incorporate the EHPPV prepared by each of these routes into light-emitting diodes to compare the external quantum efficiencies of the devices with the PL quantum yields.

Experimental

Measurements

NMR spectra were recorded on Bruker AM500, AMX500, or DPX400 MHz spectrometers. ^{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) and unless otherwise stated all spectra were recorded as a solution in distilled dichloromethane. Mass spectra were recorded on either a VG Autospec or BioQ (Electrospray) spectrometer, the mode of ionisation being stated in each case. Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Microanalyses were carried out in the Inorganic Chemistry Laboratory, Oxford. 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 ($\bar{M}_p = 1300–15.4 \times 10^6$) in tetrahydrofuran with toluene as flow marker. 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 mL min^{-1}. The PL spectra of thin films were measured using a CCD spectrograph following excitation by an argon ion laser at 476 nm. The absolute photoluminescence quantum yield was measured in air using an integrating sphere to collect the light emitted in all directions[13] again with excitation at 476 nm provided by an argon ion laser. The thermogravimetric analysis was carried out on a Rheometric Scientific STA 1500. For each run the sample was held at 25 °C for 30 min and then heated from 25–600 °C at 5 °C min^{-1}. The analysis was done under nitrogen unless otherwise stated.

1,4-Bis(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene 2

A mixture of **1**[5a] (33.0 g, 141 mmol), carbon tetrachloride (686 cm^3), *N*-bromosuccinimide (55.2 g, 309 mmol), and

AIBN (6.48 g, 39.4 mmol) was heated at reflux for 4 h. The cooled reaction mixture was filtered through a plug of silica gel using carbon tetrachloride as eluent. The filtrate was collected and the solvent completely removed to yield a yellow oil (59.4 g).

A mixture of crude 1,4-bis(bromomethyl)-2-(2′-ethylhexyloxy)benzene **5** (59.4 g), glacial acetic acid (500 cm^3), and anhydrous sodium acetate (55.9 g, 681 mmol) was heated at reflux for 5 h under nitrogen. The resultant mixture was allowed to cool to room temperature and the solvent was completely removed. The residue was dissolved in dichloromethane (400 cm^3), washed with water (200 cm^3), dried over anhydrous magnesium sulfate, filtered, and the solvent completely removed to give a brown oil. A preliminary purification was carried out using column chromatography over silica using ethyl acetate–light petroleum (1 : 30) as eluent to give a fraction which consisted mainly of the bis-acetate which was recovered as a yellow oil (30.7 g).

A mixture of the crude 1,4-bis(acetoxymethyl)-2-(2′-ethylhexyloxy)benzene (30.7 g), methanol (189 cm^3), dichloromethane (84 cm^3), and aqueous potassium hydroxide (10 M, 84 cm^3) was stirred at room temperature overnight. The solvent was completely removed and the residue was added to a mixture of dichloromethane (450 cm^3) and brine (300 cm^3). The organic layer was separated and washed with water (2×300 cm^3). The combined water layers were extracted with dichloromethane (2×200 cm^3). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and solvent completely removed to give an orange oil. The residue was purified by column chromatography over silica gel using ethyl acetate–dichloromethane (0 : 1 to 1 : 5) as eluent to give a yellow oil of **2** (17.3 g, 46%). (Found: C, 72.2; H, 9.6. $C_{16}H_{26}O_3$ requires C, 72.1; H, 9.8%); ν_{max}/cm^{-1} (neat) 3336 (OH); λ_{max}/nm 277sh ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 2507) and 283 (2664); δ_H(400 MHz; $CDCl_3$) 0.89–0.97 (6 H, m, 2 × Me), 1.31–1.38 (4 H, m, 2 × CH_2), 1.41–1.54 (4 H, m, 2 × CH_2), 1.65–1.82 (2 H, m, OH and CH), 2.35 (1 H, m, OH), 3.94 (2 H, m, $ArOCH_2$), 4.68–4.70 (4 H, m, 2 × $ArCH_2$), 6.91 (1 H, d, *J* 7.5, ArH), 6.95 (1 H, s, ArH), and 7.26 (1 H, d, *J* 7.5, ArH); δ_C(100 MHz; $CDCl_3$) 11.1, 14.0, 23.0, 24.1, 29.0, 30.7, 39.4, 62.1, 65.3, 70.2, 109.5, 118.6, 128.5, 128.6, 141.9, and 157.3; *m/z* [CI(NH_3)] 266 (M^+).

1,4-Bis(chloromethyl)-2-(2′-ethylhexyloxy)benzene 3

DMAP (1.42 g, 11.7 mmol), tosyl chloride (6.05 g, 31.7 mmol), and distilled triethylamine (2.7 cm^3, 19.5 mmol) were added sequentially to a solution of **2** (1.51 g, 5.66 mmol) in dichloromethane (38 cm^3) under argon at room temperature. The reaction mixture was stirred at room temperature for 3.5 h and then filtered through a plug of silica gel using dichloromethane as eluent. The filtrate was collected and solvent completely removed to give a yellow solid. The residue was purified by column chromatography over silica using light petrolum as eluent. The main fraction was collected and the solvent completely removed to give **3** as a colourless oil, which solidified at low temperatures (1.00 g, 58%) (Found: C, 63.3; H, 7.7. $C_{16}H_{24}Cl_2O$ requires C, 63.4; H, 8.0%); λ_{max}/nm 289 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 4763); δ_H(400 MHz; $CDCl_3$) 0.91–0.98 (6 H, m, 2 × Me), 1.33–1.39 (4 H, m, 2 × CH_2), 1.44–1.61 (4 H, m, 2 × CH_2), 1.76–1.83 (1 H, m, CH), 3.94 (2 H, d, *J* 5.5, $ArOCH_2$), 4.58 (2 H, s, CH_2Cl), 4.65 (2 H, s, CH_2Cl), 6.93–6.96 (2 H, m, ArH), and 7.34 (1 H, d, *J* 7.5, ArH); δ_C(100 MHz; $CDCl_3$) 11.2, 14.1, 23.0, 24.0, 29.1, 30.6, 39.5, 41.3, 46.1, 70.3, 111.5, 120.3, 126.2, 130.6, 139.3, and 157.2; *m/z* [CI(NH_3)] 302, 304, and 306 (M^+); HRMS 302.1214 (302.1204 calc. mass).

Poly{[2-(2′-ethylhexyloxy)-1,4-phenylene](1-chloroethylene)} 7

A mixture of potassium *tert*-butoxide (298 mg, 2.65 mmol) in dry tetrahydrofuran (14 cm^3) was added to a solution of **3** (868 mg, 2.86 mmol) in dry tetrahydrofuran (22 cm^3) which had been cooled in an ice bath under argon. The reaction was stirred with ice bath cooling for 1 h before being poured into methanol (60 cm^3). The reaction mixture was centrifuged for 10 min at 4500 rpm. The supernatant was removed and the residue was dissolved in tetrahydrofuran (62 cm^3). The polymer solution was then added to propan-2-ol (84 cm^3) and the mixture was centrifuged at 4500 rpm for 10 min. The supernatant was removed and the yellow precipitate of **7** (~437 mg, ~57%) was dissolved in tetrahydrofuran (93 cm^3), δ_H(400 MHz; $CDCl_3$) 0.91 (3 H, br m, Me), 0.97 (3 H, br t, Me), 1.25–1.40 (4 H, br s, 2 × CH_2), 1.43–1.60 (4 H, br m, 2 × CH_2), 1.72–1.83 (1 H, br m, CH), 3.18–3.30 (1 H, br m, $ArCH_2$), 3.31–3.45 (1 H, br m, $ArCH_2$), 3.82–4.03 (2H, br m, $ArOCH_2$), 5.15–5.24 (1 H, br s, CHCl), 6.82–6.95 (2 H, br m, ArH), and 7.01–7.15 (1 H, br m, ArH); GPC (0.35 mg cm^{-3}, 24.5 °C), $\bar{M}_n \sim 3.4 \times 10^5$, $\bar{M}_w \sim 1.6 \times 10^6$, polydispersity index ~4.7 or $\bar{M}_n$ 2.5×10^5, $\bar{M}_w$ 4.4×10^5, polydispersity index 1.8 after disaggregation; thermogravimetric analysis: 234 °C (weight loss: 10%; expected: 14%).

1,4-Bis[(methylthio)thiocarbonyloxymethyl]-2-(2′-ethylhexyloxy)benzene 4

A mixture of **2** (100 mg, 0.38 mmol) anhydrous tetrahydrofuran (3 cm^3) and sodium hydride (60% dispersion in oil, 45 mg, 1.13 mmol) was stirred at room temperature under argon for 1.5 h. Carbon disulfide (0.1 cm^3, 1.50 mmol) was added to the reaction mixture which was then stirred for another 3 h. Iodomethane (0.14 cm^3, 2.25 mmol) was added and the reaction mixture was stirred for a further 4 h. The reaction mixture was passed through a plug of silica gel using ether as eluent. The filtrate was collected and the solvent completely removed to give a yellow oil. The residue was purified by chromatotron chromatography over silica using ethyl acetate–light petroleum (0 : 1 to 1 : 6) giving a pale yellow oil, which solidified at low temperature, of **4** (110.3 mg, 66%), (mp 33–34 °C) (Found: C, 53.7; H, 7.0. $C_{20}H_{30}O_3S_4$ requires C, 53.4; H, 6.8%); ν_{max}/cm^{-1} (neat) 965, 1056, and 1195 (br); λ_{max}/nm 281 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 22384); δ_H(500 MHz; $CDCl_3$) 0.89–0.96 (6 H, m, 2 × Me), 1.30–1.35 (4 H, m, 2 × CH_2), 1.38–1.53 (4 H, m, 2 × CH_2), 1.69–1.78 (1 H, m, CH), 2.57 (3 H, s, SMe), 2.60 (3 H, s, SMe), 3.90 (2 H, d, *J* 5.5, $ArOCH_2$), 5.61 (2 H, s, $ArCH_2$), 5.66 (2 H, s, $ArCH_2$), 6.93 (1 H, d, *J* 1.0, ArH), 6.99 (1 H, dd, *J* 1.0 and 7.5, ArH), and 7.37 (1 H, d, *J* 7.5, ArH); δ_C(100 MHz; $CDCl_3$) 11.2, 14.1, 19.0 (SMe), 19.2 (SMe), 23.0, 23.9, 29.1, 30.6, 39.4 (CH), 70.3, 70.8, 74.9, 111.2, 120.1, 123.6, 130.4, 136.8, 157.6, 215.6 (C=S), and 215.7 (C=S); *m/z* [Electrospray (NH_3)] 465 (MNH_4^+) and 339 [M − OC(S)SMe]; HRMS 339.1448 [339.1452 calc. mass for M − OC(S)SMe].

Poly([2-(2′-ethylhexyloxy)-1,4-phenylene]{1-[(methylthio)thiocarbonyloxy]ethylene}) 8

A mixture of potassium *tert*-butoxide (45 mg, 0.40 mmol) in dry tetrahydrofuran (2.5 cm^3) was added to a solution of **4** (182 mg, 0.43 mmol) in dry tetrahydrofuran (3 cm^3) cooled in an ice bath under argon. The reaction mixture was stirred with ice bath cooling for 1 h and then poured onto methanol (9.6 cm^3). The reaction mixture was concentrated to about two thirds of its original volume under reduced pressure and then centrifuged for 10 min at 4500 rpm. The supernatant was removed and the resultant yellow residue of **8** (~53 mg, ~38%) was dissolved in tetrahydrofuran (3 cm^3), ν_{max}(film on KBr disc)/cm^{-1} 967, 1060 and 1217; δ_H(400 MHz; $CDCl_3$) 0.77–1.03 (3 H, br m, 2 × Me), 1.17–1.87 (br m, CH and CH_2), 2.03, 2.20, 2.55, 2.80–3.33, and 3.57–4.04 (SMe, $ArCH_2$, OCH_2), 4.59–4.70 and 4.87–5.68 (ArCH), and 6.39–7.65 (ArH and vinylH); GPC (0.80 mg cm^{-3}, 22.6 °C), $\bar{M}_n = 4.7 \times 10^3$, $\bar{M}_w = 8.5 \times 10^3$, polydispersity index = 1.6; thermogravimetric analysis: 125 °C (weight loss: 12%; expected: 32%).

1,4-Bis(bromomethyl)-2-(2′-ethylhexyloxy)benzene 5

Phosphorus tribromide (0.8 cm^3, 8.41 mmol) was added dropwise to a solution of **2** (852 mg, 3.20 mmol) in dry dichloromethane (60 cm^3) at room temperature under argon. The reaction mixture was stirred at room temperature for 18 h and then poured onto an ice–water mixture (30 cm^3). The organic layer was separated, washed with water (2×30 cm^3), brine (1×30 cm^3), dried over anhydrous magnesium sulfate, and the solvent completely removed to give a yellowish oil. The residue was purified by column chromatography over silica with ethyl acetate–light petroleum (1 : 30) as eluent to give a colourless oil, which crystallised at low temperatures, of **5** (1.05 g, 84%); mp 43–44 °C (Found: C, 49.4; H, 6.5. $C_{16}H_{24}Br_2O$ requires C, 49.0; H, 6.2%); λ_{max}/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 11065) and 301 (5042); δ_H(400 MHz; $CDCl_3$) 0.90–1.01 (6 H, m, $2 \times Me$), 1.32–1.42 (4 H, m, $2 \times CH_2$), 1.43–1.65 (4 H, m, $2 \times CH_2$), 1.77–1.84 (1 H, m, CH), 3.95 (2 H, d, *J* 5.5, $OC\mathit{H}_2CH$), 4.47 (2 H, s, $ArCH_2$), 4.54 (2 H, s, $ArCH_2$), 6.91 (1 H, d, *J* 1.5, ArH), 6.93 (1 H, dd, *J* 1.5 and 7.5, ArH), and 7.29 (1 H, d, *J* 7.5, ArH); δ_C(100 MHz; $CDCl_3$) 11.3, 14.1, 23.0, 24.0, 28.4, 29.1, 30.6, 33.4, 39.5, 70.3, 112.0, 120.8, 126.5, 131.0, 139.8, and 157.2; *m/z* [CI(NH_3)] 408, 410, and 412 (MNH_4^+), and 390, 392, and 394 (M^+).

1,4-Bis[ethoxy(thiocarbonyl)thiomethyl]-2-(2′-ethylhexyloxy)benzene 6

A mixture of **5** (92 mg, 0.23 mmol), potassium *O*-ethyl xanthate (94 mg, 0.59 mmol), tetra-*n*-butylammonium bromide (21 mg, 0.07 mmol), and dry dichloromethane (3 cm^3) was stirred at room temperature for 4 h under argon. The reaction mixture was filtered through a plug of silica gel using dichloromethane as eluent. The filtrate was collected and the solvent completely removed to give a colourless oil. The oil was purified by chromatotron chromatography over silica using ethyl acetate–light petroleum (1 : 30) as eluent. The main fraction was collected and the solvent completely removed to give **6** as a colourless oil (108 mg, 98%) (Found: C, 55.5; H, 7.7. $C_{22}H_{34}O_3S_4$ requires C, 55.7; H, 7.2%); ν_{max}/cm^{-1} (neat) 1049 and 1215; λ_{max}/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 36399); δ_H(500 MHz; $CDCl_3$) 0.92–0.97 (6 H, m, $2 \times Me$), 1.32–1.40 (4 H, m, $4 \times CH_2$), 1.42–1.44 (6 H, t, *J* 7.1, $2 \times OCH_2C\mathit{H}_3$), 1.52–1.59 (4 H, m, $2 \times CH_2$), 1.72–1.80 (1 H, m, CH), 3.89 (2 H, d, *J* 5.5, $ArOCH_2$), 4.35 (2 H, s, CH_2S), 4.38 (2 H, s, CH_2S), 4.64–4.70 (4 H, m, $2 \times OC\mathit{H}_2Me$), 6.86–6.88 (2 H, m, ArH), and 7.31 (1 H, m, ArH); δ_C(125 MHz; $CDCl_3$) 11.2, 13.72, 13.75, 14.0, 23.0, 24.0, 29.0, 30.6, 35.2, 39.4, 40.5, 69.7, 70.0, 70.1, 111.7, 120.6, 123.7, 130.5, 136.6, 157.1, 213.8, and 214.8; *m/z* [Electrospray (NH_3)] 492 (MNH_4^+).

Poly(2-(2′-ethylhexyloxy)-1,4-phenylene]{1-[ethoxy(thiocarbonyl)thio]ethylene}) 9

A mixture of potassium *tert*-butoxide (153 mg, 1.37 mmol) and dry tetrahydrofuran (7.6 cm^3) was added to a solution of **5** (700 mg, 1.47 mmol) in dry tetrahydrofuran (11 cm^3) cooled in an ice bath under argon. The reaction mixture was stirred with ice bath cooling for 1 h before being poured into methanol (20 cm^3). The mixture was centrifuged for 10 min at 4500 rpm and the supernatant was removed. The residue was dissolved in tetrahydrofuran (10 cm^3) and then added to propan-2-ol (20 cm^3). The mixture was centrifuged at 4500 rpm for 10 min and the supernatant removed. The yellow residue of **9** (~354 mg, ~68%) was dissolved in tetrahydrofuran (13 cm^3), ν_{max}(film on KBr disc)/cm^{-1} 1049 and 1219; λ_{max}/nm (thin film) 289; δ_H(400 MHz; $CDCl_3$) 0.85–0.92 (3 H, br m, Me), 0.94–1.01 (3 H, br m, Me), 1.14–1.68 (11 H, $4 \times CH_2$ and $OCH_2C\mathit{H}_3$), 1.72–1.83 (1 H, br m, CH), 2.95–3.12 (1 H, br m, $ArCH_2$), 3.18–3.32 (1 H, br m, $ArCH_2$), 3.71–3.98 (2 H, br m, $ArOCH_2$), 4.13–4.50 (2 H, br m, $OC\mathit{H}_2Me$), 5.07–5.12 (1 H, br m, ArCH), 6.75–6.90 (2 H, br m, ArH), and 7.00–7.09 (1 H, br s, ArH); GPC (0.81 mg cm^{-3}, 27.2 °C) $\bar{M}_n = 3.2 \times 10^5$, $\bar{M}_w = 7.7 \times 10^5$, polydispersity index 2.4, or $\bar{M}_n = 1.5 \times 10^5$, $\bar{M}_w = 2.6 \times 10^5$, polydispersity 1.7 after disaggregation; thermogravimetric analysis (air) 236 °C (weight loss: 31%; expected: 34%).

Poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] 10

Method 1. Thin films of **7** were heated at 213 °C at 0.01 mmHg for 15 h to give **10**; ν_{max} (film on KBr disc)/cm^{-1} 966 and 3056; λ_{max}(thin film)/nm 210, 256, 328sh, and 450.

Method 2. Thin films of **8** were heated at 218 °C at 0.01 mmHg for 12 h to give **10**; ν_{max} (film on KBr disc)/cm^{-1} 966 and 3055; λ_{max}(thin film)/nm 208, 256sh, 335sh, and 417.

Method 3. Thin films of **9** were heated at 209 °C at <0.01 mmHg for 15 h to give **10**; ν_{max} (film on KBr disc)/cm^{-1} 965 and 3054; λ_{max}(thin film)/nm 210, 258, 332sh, and 445.

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