JOURNAL OF
Materials
CHEMISTRY

Comparison of precursor polymer routes to and electronic properties of a new phenylacetylene derivatised poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene]

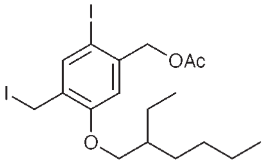
Shih-Chun Lo,[a] Anna K. Sheridan,[b] Ifor D. W. Samuel[b] and Paul L. Burn*[a]

[a] *The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QY*
[b] *Department of Physics, University of Durham, South Road, Durham, UK DH1 3LE*

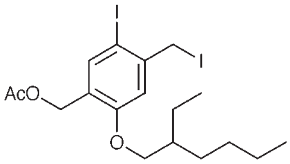
Received 27th May 1999, Accepted 25th October 1999

We have prepared poly[2-(2′-ethylhexyloxy)-5-phenylethynyl-1,4-phenylenevinylene] (PAPPV) **13** *via*, *S*-methyl xanthate **10**, chloro **11**, and *O*-ethyl xanthate **12** precursor polymers. All three precursor polymers could be thermally converted to give films of **13**. We found that the UV–VIS and photoluminescence (PL) spectra, and PL quantum yields (11–14%) were similar when **13** was prepared from either the *S*-methyl xanthate or chloro precursor polymers. In contrast, the UV–VIS and PL spectra of **13** prepared via the *O*-ethyl xanthate precursor polymer were observed to be blue-shifted and the PL quantum yield was much lower (2%).

Poly(1,4-phenylenevinylene) (PPV) and its derivatives have been studied extensively with particular emphasis in recent years on their use as the light-emitting layers in light-emitting diodes (LEDs).[1] The main derivatives of PPV usually have one or more alkoxy or alkyl substituents of varying lengths attached to the phenyl ring.[2] Other phenyl substituents that have also been studied include halogen,[1b,3] thioether,[4] aryl,[5] styryl,[6] and silyl.[1b] However, the effects of a side-chain acetylene group on the electronic properties of a PPV derivative have yet to be explored although there have been studies on poly(1,4-phenylacetylene)s.[7] The two main synthetic routes to PPV have involved the synthesis of soluble conjugated derivatives, which are normally substituted with long lipophilic groups, or a precursor polymer route which generally leads to insoluble polymers. 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. Here, we describe the syntheses of a phenylacetylene substituted polymer, poly{[2-(2′-ethylhexyloxy)-5-phenylacetylenyl-1,4-phenylenevinylene]} (PAPPV) **13**, *via* chloro, *S*-methyl xanthate, and *O*-ethyl xanthate precursor polymers, and compare its electronic properties with the unsubstituted parent poly[2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (EHPPV)[8] prepared *via* the equivalent precursor polymers.



14



15

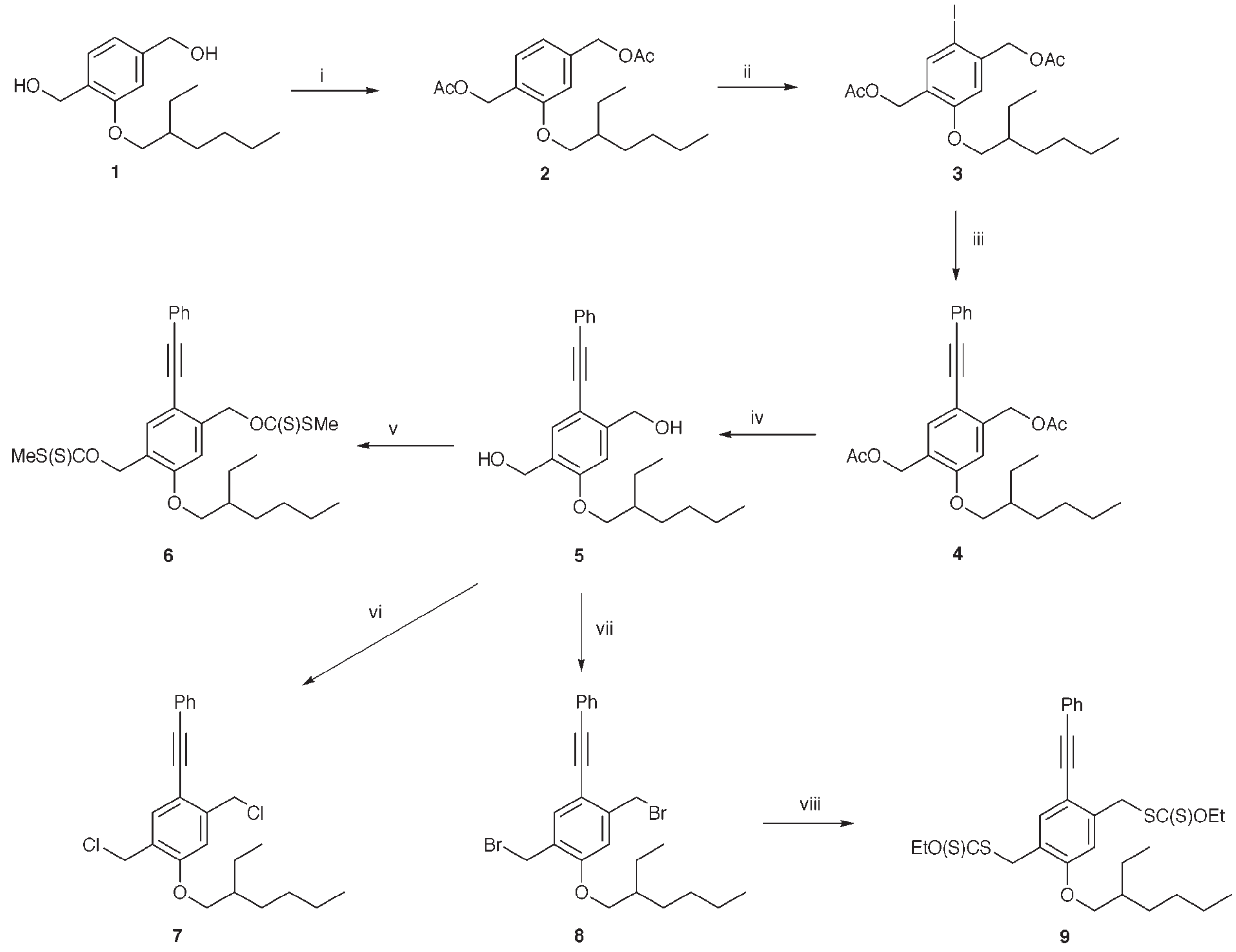
Results and discussion

Monomer syntheses

The strategies for the syntheses of the three monomers for the preparation of PAPPV **13** are shown in Scheme 1. The first step in all three syntheses was acetylation of bis-hydroxy **1**[8] which was done to facilitate the handling of the products in the next two steps. **1** was acetylated in a 97% yield using acetic anhydride in pyridine heated at reflux. The next step in the synthesis was the addition of iodine and this proved to be more problematic. Introduction of the iodo group onto **2** was first attempted using iodine in a mixture of periodic acid, glacial acetic acid and aqueous sulfuric acid. Under these conditions a small amount (27%) of the desired iodonated compound **3** was isolated. In addition to **3** we also formed an inseparable mixture of **14** and **15** which were not only iodonated on the aromatic ring but also on one benzylic position and these were isolated in yields of around 34%. Although **14** and **15** could be re-acetylated in good yield this approach was inefficient. We have found that excellent yields of **3** can be achieved by treatment of a chloroform solution of **2** with iodine and silver acetate at room temperature. Under these mild conditions **3** can be formed in yields of up to 97%. Addition of the phenylacetylene moiety to give **4** was achieved by reacting **3** with an excess of copper(I) phenylacetylide. Under these conditions **4** could be formed in a 93% yield. The acetate protecting groups were then removed by treating **4** with aqueous hydroxide to give **5** in 96% yield. The bis-*S*-methyl xanthate monomer **6** was formed in 56% yield by sequential treatment of **5** with sodium hydride followed by carbon disulfide, and then methyl iodide. **5** was also converted to the bis-chloro monomer **7** in up to 90% yield by reaction with a mixture of DMAP, *p*-toluenesulfonyl chloride and triethylamine. Finally, to prepare the *O*-ethyl xanthate monomer **9**, **5** was first transformed with phosphorus tribromide to the bis-bromo monomer **8** (in 49% yield) which was then reacted with potassium *O*-ethyl xanthate to give **9** in 96% yield.

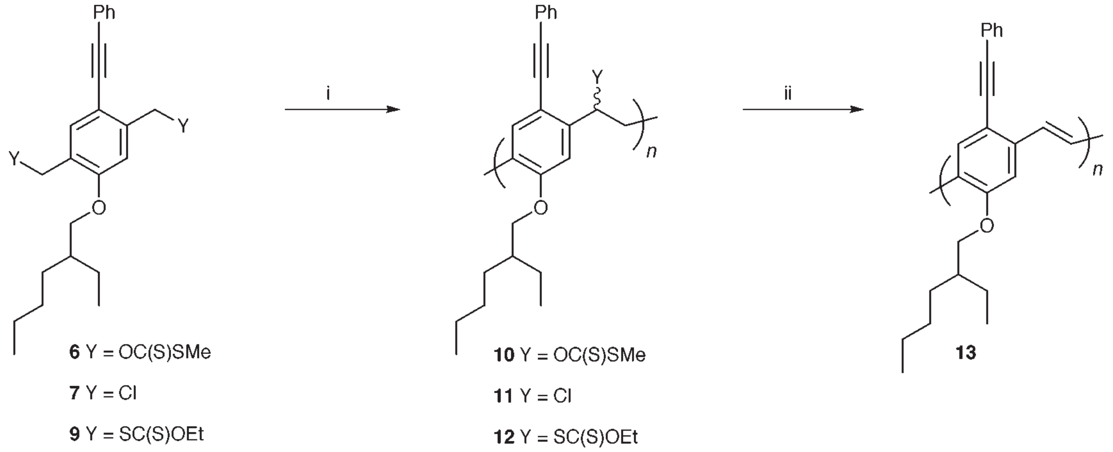
Polymerisations and conversions

The polymerisations of all three polymers were carried out under similar conditions (Scheme 2). The general procedure involved the treament of a 0.13 M tetrahydrofuran solution of monomer with *ca.* 0.9 equivalents of a 0.18–0.19 M tetrahydrofuran solution of potassium *tert*-butoxide. The reactions were stirred with ice-bath cooling for 1 h before being quenched by precipitation into methanol. Under these conditions the *S*-methyl xanthate polymer **10**, the chloro polymer **11**, and the *O*-ethyl xanthate polymer **12** were formed in yields of *ca.* 26, 80 and 60%, respectively. The molecular weights of dilute solutions of the three precursor polymers were analysed by gel-permeation chromatography (GPC) (against polystyrene standards) immediately on dilution and after equilibration. The samples were equilibrated by being treated in an ultrasonic



Scheme 1 *Reagents and conditions:* i, acetic anhydride, pyridine, heat, N_2 ; ii, I_2, AgOAc, $CHCl_3$, room temp.; iii, PhCCCu, pyridine, heat, N_2; iv, NaOH, H_2O, MeOH, CH_2Cl_2, room temp., Ar; v, NaH, diethyl ether, heat, then CS_2, heat, then MeI, heat, Ar; vi, DMAP, tosyl chloride, triethylamine, CH_2Cl_2, room temp., N_2; vii, PBr_3, diethyl ether, room temp., Ar; viii, potassium *O*-ethyl xanthate, $(n\text{-Bu})_4NBr$, CH_2Cl_2, Ar, room temp.

bath for 10 min. Under these equilibration conditions we observed a drop in $\bar{M}_w$ for the chloro and *O*-ethyl xanthate precursor polymers without any polymer degradation whilst the *S*-methyl xanthate precursor polymer **10** showed little change. The decrease in $\bar{M}_w$ observed by GPC analysis for **11** and **12** 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 owing to the dissociation of polymer aggregates or physical networks.[8,9] Interestingly, the *S*-methyl xanthate precursor polymer **10** was found to have an $\bar{M}_w$ of 2.9×10^5 and polydispersity of 2.2 which is significantly higher than that observed for the *S*-methyl xanthate precursor polymer to EHPPV ($\bar{M}_w$ of 8.5×10^3 and a polydispersity of 1.8) indicating that the phenylacetylene is enhancing the polymerisation process. In comparing the syntheses of **10**, **11** and **12** with their counterparts for the preparation of EHPPV two trends are notable.[8] First, the choro and *O*-ethyl xanthate monomers give higher yields of their respective precursor polymers than the *S*-methyl xanthate monomers, and second, the molecular weights of the precursor



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

polymers follow the same trend with the *S*-methyl xanthate and chloro monomers forming the polymers of lowest and highest observed molecular weights, respectively. In addition, all three precursor polymers were found to be soluble in tetrahydrofuran and chloroform with the xanthate precursor polymers being much more soluble than the chloro precursor polymer.

Thermogravimetric analysis (TGA) of polymers **10**, **11** and **12** was carried out with a heating rate of 5 °C min^{-1} under nitrogen and we assign the first weight loss observed by TGA to the elimination of the leaving group. For the *S*-methyl xanthate polymer **10**, the xanthate group was found to eliminate at 134 °C, with the first weight loss occurring at *ca.* 120 °C. The weight loss observed for **10** at this temperature was 21%, which is close to the 25% that is expected from the precursor polymer, which has low levels of conjugation. Similarly, TGA of the chloro precursor polymer **11** indicated that hydrogen chloride was eliminated at 255 °C with the elimination beginning at *ca.* 234 °C. We found that the weight loss for **11** was 9% which is near to that expected (10%) for the fully saturated precursor polymer. Finally, analysis of **12** indicated that the *O*-ethyl xanthate group was being eliminated at 229 °C with an onset of elimination of *ca.* 210 °C. The weight loss was 23% which was close to the 27% expected for the elimination of the *O*-ethyl xanthate groups from the precursor polymer.

Given that different precursor polymers to the same conjugated polymer can result in polymers with similar chemical structures but different electronic properties we were interested to determine the properties of PAPPV prepared by the three different precursor polymers. All three precursor polymers and the conjugated polymers formed after thermal conversion were studied by UV–VIS and IR spectroscopy. The UV–VIS 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. All three precursor polymers were thermally converted in the temperature range 211–213 °C under vacuum overnight.

The IR spectra of the *S*-methyl xanthate precursor polymer **10** and conjugated polymer **13** formed under these conditions are shown in Fig. 1. The important feature to note is that the absorptions at 1061 and 1214 cm^{-1} which we assign to the *S*-methyl xanthate leaving group are absent in the sample of **13**. Instead we observe a strong absorption at 964 cm^{-1} which corresponds to the *trans*-vinylene CH out-of-plane bend and an absorption at 3058 cm^{-1} which corresponds to a vinylene CH stretch. The IR spectra of the chloro precursor polymer **11** and **13** formed from **11** are shown in Fig. 2. Again the two absorptions at 964 and 3058 cm^{-1} are observed in the thermally treated sample indicating that conversion has taken place. Finally, the *O*-ethyl xanthate polymer **12** was converted to **13** and their spectra are shown in Fig. 3. The absorption at 1048 cm^{-1} which we assign to the xanthate leaving group in **12** was absent in the formed **13** and in their place we observed the absorptions which correspond to *trans*-vinylene units. At first sight the IR spectra of **13** prepared from the three different precursors look similar. However, close examination of the IR spectra of **13** formed from each of the precursor polymers shows that there are differences which are most striking in **13** prepared from **12**. The differences arise in the relative intensity of the absorption near or at 964 cm^{-1} which is one of the strong indicators of *trans*-vinylene links. When **13** was prepared from **10** or **11** the intensity of this absorption, relative to the other absorptions in the spectra, was similar (Fig. 1 and 2). In contrast, when **13** was prepared from **12** the relative intensity of the *trans*-vinylene absorption is significantly less relative to the other absorptions in the spectra (Fig. 3). In addition to the absorption at 964 cm^{-1} each of the samples also has an absorption at or near 861 cm^{-1} which is close to the absorption that was assigned to *cis*-vinylene linkages in PPV prepared from an *O*-ethyl xanthate precursor polymer.[10] Therefore, as the ratio of the absorptions at 967 and 863 cm^{-1} in **13** prepared from **12** is significantly smaller than in the samples of **13** which were prepared from **10** and **11** we conclude that **13** prepared from the *O*-ethyl xanthate precursor polymer has a greater proportion of *cis*-linkages.

The thin films of **13** for UV–VIS and photoluminescence analysis were prepared so that the absorption associated with the delocalised π–π^* transitions had an optical density of around one. The effect of the different synthetic routes used on the absorption spectrum of **13** is shown in Fig. 4 which compares the absorption of thin films of **13** prepared from **10**, **11** and **12**. The spectrum of **13** prepared from **10** and **11** shows a strong absorption in the region of 470 nm, and a shorter wavelength peak in the region of 300 nm. For comparison the analogue of polymer **13** without the phenylacetylene substituent, EHPPV, has an absorption maximum at 450 nm, and the feature at 300 nm is absent.[8] This observation suggests that the 300 nm feature is due to a localised transition associated with the diphenylacetylene moiety and is consistent with the absorption spectra of the diphenylacetylene monomers. We consider that the small red-shift to 470 nm in the absorption of the phenylacetylene substituted polymer is due to a modest increase in electron delocalisation due to the phenylacetylene groups.

The absorption spectrum of **13** prepared from **12** differs from that obtained by the other two precursor routes: both the onset and first peak of the absorption are blue-shifted by between 40 and 50 nm (0.2–0.3 eV). Two possible reasons for this blue-shift are that the polymer has an increased level of *cis*-linkages or that there has only been partial conversion of **12** to **13**. Both explanations would lead to reduced electron delocalisation and hence a blue-shifted spectrum. The IR analysis of **13** from **12** would suggest that the conversion had gone essentially to completion. However, the IR analysis was carried out on a film prepared by depositing a solution of the polymer onto a KBr disc and then allowing the solvent to evaporate. The sample for UV–VIS analysis was spin-coated from solution and hence the film would be expected to be thinner than that used for the IR analysis. Given that trapped elimination products, which might occur in thicker films, can act as catalysts for elimination of remaining leaving groups[11] we also investigated a thin film of **13** prepared by converting **12** which had been spin-coated onto a KBr disc under the same conditions used for the preparation of the UV–VIS sample. IR analysis of the 'spin-coated' sample of **13** also showed that the xanthate leaving group had been eliminated and we therefore propose that the blue shift in the UV–VIS absorption spectra is due to increased *cis*-linkages. This is in contrast to the synthesis of EHPPV where the UV–

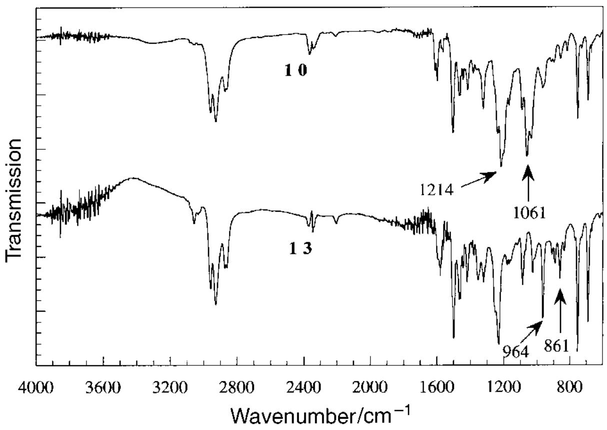


Fig. 1 IR spectra of films of **10** and **13** formed from **10**.

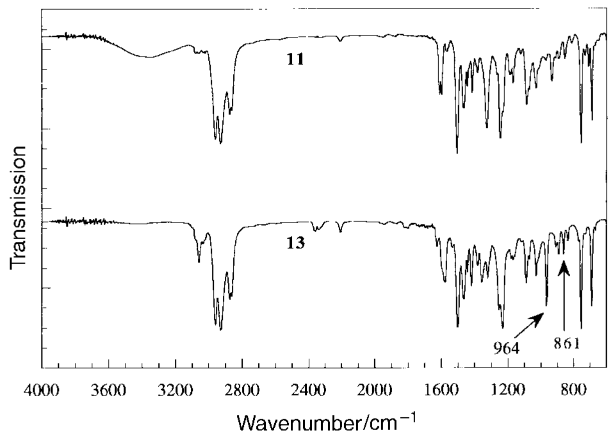


Fig. 2 IR spectra of films of **11** and **13** formed from **11**.

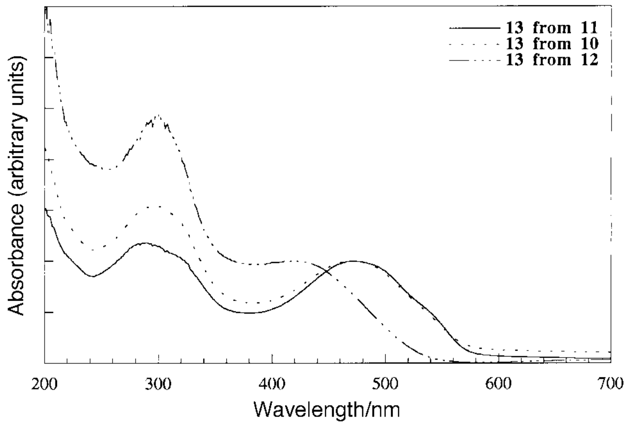


Fig. 4 UV–VIS absorption spectra of films of **13** formed from **10**, **11** and **12**.

VIS absorption spectra was the same whether the EHPPV was prepared from the chloro or *O*-ethyl xanthate route and this clearly shows that the phenylacetylene moiety is having an important effect on the conversion process.

Photoluminescence (PL) spectra give further information about the electronic structure of polymers. The samples of **13** for the PL studies were prepared by heating the precursor polymers at 220 °C at <0.001 mBar for 15.5 h. PL spectra of **13** prepared by each of the three precursor routes are shown in Fig. 5. All the spectra are very broad (150 nm full width at half maximum) with only weak structure. The spectrum of **13** prepared from **11** peaks at 680 nm (1.8 eV), close to the peak of 665 nm (1.9 eV) for **13** prepared from **10**. In contrast, the use of precursor **12** to make **13** leads to a large blue-shift of the PL which then peaks at 580 nm (2.1 eV). The blue-shift in the UV–VIS absorption and PL spectra of **13** prepared from **12** are of similar size.

The PL spectra are also remarkably different from those of EHPPV, which does not have the phenylacetylene substitution, prepared from the analogues of **10**–**12**. The unsubstituted materials showed pronounced vibronic structure with peaks/shoulders close to 555, 600 and 650 nm.[8] The PL of **13** prepared from **10** and **11** is much redder than that of EHPPV with the red shift in PL being larger than the red shift in the absorption spectra. In fact the position and shape of the emission spectra of **13** prepared from **10** or **11** resemble the emission from a dihexyloxycyano-substituted PPV (CN-PPV) which has a broad structureless emission peaking at 690 nm,[12] although the phenylacetylene materials give a little more emission at short wavelengths (<550 nm).

It has been shown that the broad, red-shifted and long-lived PL from CN-PPV films is due to an intermolecular excited state such as an excimer.[12] In general it has been proposed that light emission in conjugated polymers arises from both intra- and inter-molecular excited states, with interconversion between them.[13] This model provides a possible framework for understanding the observed behaviour. It may be that substantial intermolecular emission is observed in **13** prepared from **10** and **11**, whereas as in **13** prepared from **12** there is much more light emission from an intramolecular excited state. The differences in the observed spectra would then be due to differences in the arrangement of the polymer chains due to the syntheses used. In the case of **13** prepared from **12** the higher density of *cis*-linkages may reduce contact between polymer chains, thereby impeding the formation of intermolecular excitations. Further photophysical studies would be needed to confirm this conjecture.

Finally, we have also studied the effect of synthetic route on the efficiency of PL from the resulting polymer. The PL quantum yields of PAPPV **13** formed from **10**, **11** and **12** are 14±2, 11±2, and 2±1%, respectively. These quantum yields are significantly lower than those observed for EHPPV prepared from the *S*-methyl xanthate (37±4%), chloro (55±5%) and *O*-ethyl xanthate (17±2%) precursor polymers,[8] suggesting that the phenylacetylene moiety may in some way assist in quenching the luminescence. It is also worth noting that the *O*-ethyl xanthate precursor polymer forms the least luminescent EHPPV and PAPPV.

In conclusion, we have synthesised a new phenylacetylene substituted 2-alkoxyPPV, PAPPV, *via* a chloro and two different xanthate precursor polymer routes and again clearly demonstrated that the electronic properties of PPV derivatives are very sensitive to the mode of preparation and the attachment of functional groups.

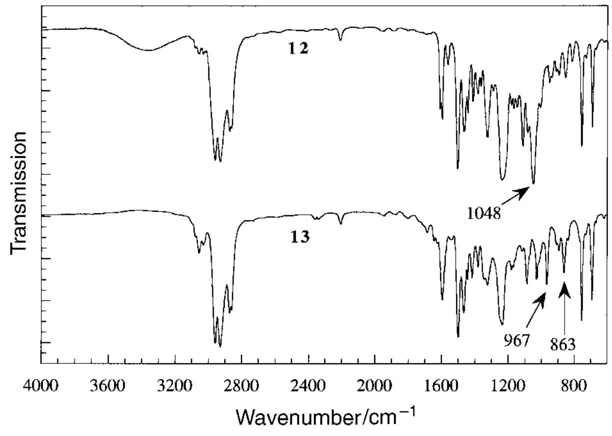


Fig. 3 IR spectra of films of **12** and **13** formed from **12**.

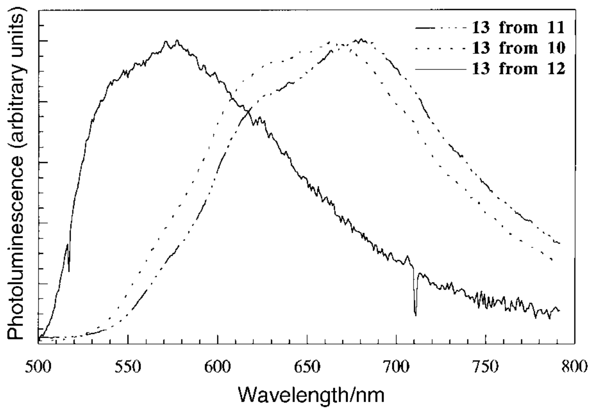


Fig. 5 Photoluminescence spectra of films of **13** formed from **10**, **11** and **12**.

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 in chloroform unless otherwise stated. UV–VIS spectra were recorded on a Perkin-Elmer UV–VIS (Lambda 14P) spectrophotometer and unless otherwise stated all spectra were recorded as a solution in distilled 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 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 ($\bar{M}_p = 1{,}300$–15.4×10^6) 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[14] 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 to 600 °C at 5 °C min^{-1} with analysis done under nitrogen.

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

A mixture of 1,4-bis(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene **1**[8] (10.13 g, 38.02 mmol), acetic anhydride (7.9 cm^3, 83.64 mmol), and distilled pyridine (22.8 cm^3) was heated under nitrogen at reflux for 4.5 h. After being cooled, the reaction mixture was added to a mixture of diethyl ether (70 cm^3) and hydrochloric acid (3.0 M, 50 cm^3). The organic layer was separated and washed with a saturated aqueous sodium hydrogen carbonate solution (2 × 50 cm^3). The aqueous layer was collected and extracted with diethyl ether (70 cm^3). The combined organic layers were dried over magnesium sulfate, filtered, and the solvent completely removed to give a brown oil (13.16 g). The residue was purified by column chromatography over silica using ethyl acetate–light petroleum (60–80 °C) (1 : 30 to 1 : 15) as eluent to give **2** as an oil (12.95 g, 97%) (Found: C, 68.3; H, 8.3. $C_{20}H_{30}O_5$ requires C, 68.5; H, 8.6%); ν_{max}/cm^{-1} (neat) 1743 (C=O); λ_{max}/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 3043); δ_H(400 MHz, $CDCl_3$) 0.89–0.95 (6 H, m, 2 × Me), 1.28–1.37 (4 H, m, 2 × CH_2), 1.37–1.57 (4 H, m, 2 × CH_2), 1.68–1.77 (1 H, m, CH), 2.10 (3 H, s, COMe), 2.11 (3 H, s, COMe), 3.86–3.94 (2 H, m, ArOCH_2), 5.09 (2 H, s, ArCH_2), 5.15 (2 H, s, ArCH_2), 6.88 (1 H, s, ArH), 6.93 (1 H, dd, *J* 1.0 and 7.6 Hz, ArH) and 7.30 (1 H, d, *J* 7.6 Hz, ArH); δ_C(125 MHz, $CDCl_3$) 11.2, 14.1, 21.00, 21.02, 23.0, 23.9, 29.1, 30.6, 39.4, 61.7, 66.2, 70.1, 111.0, 119.9, 124.3, 129.8, 137.5, 157.3, 170.8 and 170.9; *m/z* [CI(NH_3)] 368 (MNH_4^+).

2,5-Bis(acetoxymethyl)-4-(2′-ethylhexyloxy)iodobenzene 3

A solution of **2** (16.7 g, 47.6 mmol) in chloroform (20 cm^3) was added to a mixture of silver acetate (8.87 g, 53.3 mmol) iodine (13.4 g, 53.3 mmol), and chloroform (64 cm^3) which had been stirred at room temperature for 1 h under nitrogen. The reaction mixture was stirred at room temperature for 3.5 h before being passed through a plug of silica gel using dichloromethane as eluent. The filtrate was collected and washed with an aqueous solution of sodium metabisulfite (7.9 M, 100 cm^3), dried over anhydrous magnesium sulfate, filtered, and the solvent completely removed to give a yellow oil. The residue was purified by column chromatography over silica using ethyl acetate–light petroleum (60–80 °C) (0 : 1 to 1 : 30) as eluent to give a colourless oil of **3** (22.0 g, 97%), which crystallised on cooling, mp 34 °C; (Found: C, 50.4; H, 6.1. $C_{20}H_{29}IO_5$ requires C, 50.4; H, 6.1%); ν_{max}/cm^{-1} 1737 (C=O); λ_{max}/nm 290 (ε/dm^3 mol^{-1} cm^{-1} 2382); δ_H(500 MHz, $CDCl_3$) 0.89–0.94 (6 H, m, 2 × Me), 1.29–1.35 (4 H, m, 2 × CH_2), 1.39–1.52 (4 H, m, 2 × CH_2), 1.70–1.76 (1 H, m, CH), 2.11 (3 H, s, COMe), 2.15 (3 H, s, COMe), 3.86–3.91 (2 H, m, ArOCH_2), 5.09 (2 H, s, ArCH_2), 5.10 (2 H, s, ArCH_2), 6.93 (1 H, s, ArH) and 7.73 (1 H, s, ArH); δ_C(125 MHz, $CDCl_3$) 11.1, 14.0, 20.92, 20.94, 23.0, 23.9, 29.1, 30.5, 39.3, 60.7, 70.1, 70.4, 86.2, 112.8, 126.6, 139.2, 139.5, 157.4, 170.6 and 170.7; *m/z* [CI(NH_3)] 494 (MNH_4^+) and 476 (M^+).

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

A mixture of **3** (5.73 g, 476 mmol), copper(I) phenylacetylide[15] (5.33 g, 32.4 mmol) and distilled pyridine (75 cm^3) was heated at reflux for 9.5 h under nitrogen. The reaction mixture was allowed to cool and then the solvent was removed. The residue was dissolved in dichloromethane (100 cm^3) and passed through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent completely removed. The residue was purified by column chromatography over silica using ethyl acetate–light petroleum (60–80 °C) (1 : 40 to 1 : 30) as eluent to afford a yellowish oil of **4** (5.01 g, 93%) (Found: C, 74.8; H, 7.8. $C_{28}H_{34}O_5$ requires C, 74.6; H, 7.6%); ν_{max}/cm^{-1} (neat) 1739 (C=O); λ_{max}/nm 296 (ε/dm^3 mol^{-1} cm^{-1} 34817) and 314 (28263); δ_H(400 MHz, $CDCl_3$) 0.90–0.97 (6 H, m, 2 × Me), 1.31–1.37 (4 H, m, 2 × CH_2), 1.40–1.56 (4 H, m, 2 × CH_2), 1.71–1.80 (1 H, m, CH), 2.13 (3 H, s, COMe), 2.14 (3 H, s, COMe), 3.93–3.95 (2 H, m, ArOCH_2), 5.15 (2 H, s, ArCH_2), 5.34 (2 H, s, ArCH_2), 6.95 (1 H, s, ArH), 7.33–7.38 (3 H, m, 3 × Ar′H), and 7.51–7.54 (3 H, m, 2 × Ar′H and ArH); δ_C(100 MHz, $CDCl_3$) 11.2, 14.1, 21.0, 23.0, 23.9, 29.1, 30.5, 39.4, 61.2, 64.8, 70.4, 86.4 (C≡C), 92.9 (C≡C), 111.4, 114.4, 123.3, 124.6, 128.4, 128.3, 131.4, 133.2, 139.1, 157.2 (C=O), and 170.8 (C=O); *m/z* [CI(NH_3)] 468 (MNH_4^+) and 450 (M^+).

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

A mixture of **4** (3.57 g, 7.92 mmol), aqueous sodium hydroxide (10%, 51 cm^3), dichloromethane (10 cm^3) and methanol (118 cm^3) was stirred at room temperature for 5 h under argon. The solvent was removed and the residue was dissolved in dichloromethane (100 cm^3). The organic layer was washed with water (2 × 60 cm^3), dried over anhydrous magnesium sulfate, filtered, and the solvent completely removed to give a brown oil (3.08 g). The residue was purified by column chromatography over silica using ethyl acetate–light petroleum (60–80 °C) (1 : 16 to 1 : 10 to 1 : 7) as eluent to give a white solid of **5** (2.78 g, 96%), mp 71.5–72 °C (Found: C, 78.3; H, 8.6. $C_{24}H_{30}O_3$ requires C, 78.65; H, 8.25%); ν_{max}/cm^{-1} 3606 (OH); λ_{max}/nm 297 (ε/dm^3 mol^{-1} cm^{-1} 30420) and 314 (25655); δ_H(400 MHz; $CDCl_3$) 0.88–0.96 (6 H, m, 2 × Me), 1.28–1.36 (4 H, m, 2 × CH_2), 1.38–1.52 (4 H, m, 2 × CH_2), 1.71–1.80 (1 H, m, CH), 2.50 (1 H, t, *J* 6.4 Hz, OH), 2.57 (1 H, t, *J* 6.2 Hz, OH), 3.94–3.95 (2 H, m, ArOCH_2), 4.67 (2 H, d, *J* 6.4 Hz, ArCH_2), 4.89 (2 H, d, *J* 6.2 Hz, ArCH_2), 7.03 (1 H, s, ArH), 7.32–7.37 (3 H, m, 3 x Ar′H), 7.45 (1H, s, ArH) and 7.48–7.51 (2 H, m, Ar′H); δ_C(100 MHz, $CDCl_3$) 11.1, 14.1, 23.0, 24.0, 29.0, 30.6, 39.3, 61.4, 63.7, 70.5, 86.7 (C≡C), 92.9 (C≡C), 109.6, 112.5, 123.3, 128.2, 128.4, 131.3, 131.9, 143.9 and 157.3; *m/z* [CI(NH_3)] 366 (M^+) and 349 (M−OH).

1,4-Bis[(methylthio)thiocarbonyloxymethyl]-2-(2′-ethylhexyloxy)-5-(phenylethynyl)benzene 6

A solution of **5** (2.00 g, 5.46 mmol) in dry diethyl ether (23 cm^3) was added to sodium hydride (60% in oil, 655 mg, 16.4 mmol) in dry diethyl ether (23 cm^3) under argon. The reaction mixture was heated at reflux for 1 h and then carbon disulfide (1.3 cm^3, 21.8 mmol) was added. The reaction mixture was heated at reflux for 2.7 h and then iodomethane (2.0 cm^3, 32.7 mmol) was added. The reaction mixture was heated at reflux for further 2.7 h and then allowed to cool. The reaction mixture was passed through a plug of silica using diethyl ether as eluent and the filtrate was collected and the solvent completely removed to give a yellow oil. The residue was purified by column chromatography and chromatotron over silica using ethyl acetate–light petroleum (60–80 °C) (1 : 30 and 1 : 90 respectively) to give an oil of **6**, which solidified on cooling (1.67 g, 56%), mp 53 °C (Found: C, 61.6; H, 6.3. $C_{28}H_{34}O_3S_4$ requires C, 61.5; H, 6.3%); ν_{max}/cm^{-1} 1067 and 1207; λ_{max}/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 40710), 297(sh) (32811), and 316(sh) (21874); δ_H(400 MHz, $CDCl_3$) 0.90–0.96 (6 H, m, 2 × Me), 1.31–1.36 (4 H, m, 2 × CH_2), 1.40–1.54 (4 H, m, 2 × CH_2), 1.71–1.79 (1 H, m, CH), 2.59 (6 H, s, 2 × SMe), 3.95 (2 H, d, *J* 5.4 Hz, ArOC*H*$_2$), 5.66 (2 H, s, ArC*H*$_2$), 5.85 (2 H, s, ArC*H*$_2$), 7.00 (1 H, s, ArH), 7.33–7.37 (3 H, m, Ar′H), 7.49–7.53 (2 H, m, Ar′H) and 7.58 (1 H, s, ArH); δ_C(125 MHz, $CDCl_3$) 11.2, 14.1, 19.08, 19.13, 23.0, 23.9, 29.1, 30.6, 39.3, 70.2, 70.6, 73.6, 86.1 (C≡C), 93.5 (C≡C), 111.9, 114.7, 123.1, 123.9, 128.26, 128.33, 131.5, 134.0, 138.6, 157.4, 215.4 (C=S) and 215.6 (C=S).

Poly([2-(2′-ethylhexyloxy)-1,4-phenylene]{1-[(methylthio)-thiocarbonyloxy]ethylene}) 10

A solution of potassium *tert*-butoxide in tetrahydrofuran (0.18 M, 201 mg, 1.79 mol, 10 cm^3) was added to a solution of **6** in tetrahydrofuran (0.13 M, 1.06 g, 1.94 mmol, 14.5 cm^3) cooled in an ice-bath under argon. The reaction mixture was stirred for 1 h with ice-bath cooling and then poured into methanol (30 cm^3). The mixture was centrifuged at 4500 rpm for 10 min, the supernatant was removed and the residue was dissolved in tetrahydrofuran (20 cm^3). The solution was added to propan-2-ol (30 cm^3) and the mixture was centrifuged at 4500 rpm for 10 min. The supernatant was removed and the orange precipitate of **10** (*ca.* 218 mg, *ca.* 26%) was dissolved in tetrahydrofuran (14 cm^3), ν_{max}(film on KBr disc)/cm^{-1} 1061, 1214 and 2208 (C≡C); δ_H(400 MHz, $CDCl_3$) 0.80–0.96 (6 H, br m, 2 × Me), 1.20–1.55 (8 H, br m, 4 × CH_2), 1.62–1.71 (1 H, br s, CH), 2.40–2.51 (3 H, br s, SMe), 3.17–3.33 (1 H, br m, ArC*H*$_2$), 3.39–3.59 (1H, br m, ArC*H*$_2$), 3.65–3.80 (2 H, br m, ArOC*H*$_2$), 6.75 (1 H, br m, ArC*H*), 7.07–7.18 (1 H, br s, ArH), 7.20–7.39 (4 H, br m, ArH and Ar′H) and 7.44–7.55 (2 H, br m, Ar′H); GPC (0.65 mg cm^{-3}, 23.8 °C), $M_n = 1.3 \times 10^5$, $M_w = 2.9 \times 10^5$, polydispersity index 2.2, and $M_n = 1.3 \times 10^5$, $M_w = 2.3 \times 10^5$, polydispersity index 1.8 after equilibration; thermogravimetric analysis: 136 °C (weight loss: 21%; expected: 25%).

1,4-Bis(chloromethyl)-2-(2′-ethylhexyloxy)-5-(phenylethynyl)-benzene 7

DMAP (592 mg, 4.85 mmol), *p*-toluenesulfonyl chloride (2.52 g, 13.2 mmol) and distilled triethylamine (1.1 cm^3, 8.12 mmol) were added sequentially to a solution of **5** (862 mg, 2.35 mmol) in dichloromethane (16 cm^3) under nitrogen at room temperature. The reaction mixture was stirred at room temperature for 3 h and then passed through a plug of silica using dichloromethane as eluent. The filtrate was collected and the solvent competely removed to leave a yellow oil. The residue was purified by column chromatography over silica using light petroleum (60–80 °C) as eluent giving a colourless solid of **7** (850 mg, 90%), mp 36–37 °C (Found: C, 71.5; H, 7.0. $C_{24}H_{28}Cl_2O$ requires C, 71.5; H, 7.0%); λ_{max}/nm 297 (ε/dm^3 mol^{-1} cm^{-1} 29997) and 316(sh) (22239); δ_H(400 MHz, $CDCl_3$) 0.92–1.00 (6 H, m, 2 × Me), 1.33–1.40 (4 H, m, 2 × CH_2), 1.42–1.63 (4 H, m, 2 × CH_2), 1.76–1.85 (1 H, m, CH), 3.98 (2 H, d, *J* 5.4 Hz, ArOC*H*$_2$), 4.63 (2 H, s, ArC*H*$_2$), 4.84 (2 H, s, ArC*H*$_2$), 7.02 (1 H, s, ArH), 7.34–7.40 (3 H, m, Ar′H), and 7.54–7.58 (3 H, m, 2 × Ar′H and ArH); δ_C(100 MHz, $CDCl_3$) 11.2, 14.1, 23.0, 24.0, 29.1, 30.6, 39.4, 40.7, 44.7, 70.6, 86.0 (C≡C), 93.6 (C≡C), 112.0, 114.6, 123.1, 126.4, 128.3, 128.4, 131.5, 134.1, 140.8 and 157.2; *m*/*z* [CI(NH_3)] 403, 405 and 407 (MH^+).

Poly{[2-(2′-ethylhexyloxy)-5-(phenylethynyl)-1,4-phenylene-vinylene](1-chloroethylene)} 11

A solution of potassium *tert*-butoxide in tetrahydrofuran (0.19 M, 217 mg, 1.93 mmol, 10 cm^3) was added to a solution of **7** in tetrahydrofuran (0.13 M, 840 mg, 2.08 mmol, 16.4 cm^3) which had been cooled with an ice-bath under argon. The reaction mixture was stirred for 1 h with ice-bath cooling and then poured into methanol (34 cm^3). The mixture was then centrifuged at 4500 rpm for 10 min. The supernatant was removed and the precipitate was dissolved in tetrahydrofuran (55 cm^3) and then poured into propan-2-ol (63 cm^3). The mixture was then centrifuged at 4500 rpm for 10 min and the the precipitate of **11** (*ca.* 612 mg, *ca.* 80%) was collected and dissolved in tetrahydrofuran (85 cm^3), ν_{max}(film on KBr disc)/cm^{-1} 2209 (C≡C); δ_H(400 MHz, $CDCl_3$) 0.78–0.93 (6 H, br s, 2 × Me), 1.17–1.51 (8 H, br m, 4 × CH_2), 1.63–1.77 (1 H, br s, CH), 3.14–3.38 (1 H, br d, ArC*H*$_2$), 3.38–3.62 (1 H, br d, ArC*H*$_2$), 3.64–3.95 (2 H, br m, ArOC*H*$_2$), 5.81 (1 H, br s, ArC*H*Cl), 7.00–7.11 (1 H, br m, ArH) and 7.19–7.51 (6 H, br m, ArH and Ar′H); GPC (0.53 mg cm^{-3}, 24.0 °C), $M_n > 2.4 \times 10^6$, $M_w > 7.6 \times 10^6$, polydispersity index *ca.* 3.1, and $M_n = 3.9 \times 10^5$, $M_w = 8.8 \times 10^5$, polydispersity index = 2.3 after equilibration; thermogravimetric analysis: 255 °C (weight loss: 9%; expected: 10%).

1,4-Bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-(phenylethynyl)-benzene 8

A solution of **5** (700 mg, 1.91 mmol), diethyl ether (46 cm^3), and phosphorus tribromide (0.4 cm^3, 4.20 mmol) was stirred at room temperature under argon for 1 h. The reaction mixture was poured onto an ice-water mixture (30 cm^3) and the organic layer was separated, washed with water (2 × 20 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent was complete removed to give a yellowish oil. The residue was purified by chromatotron chromatography over silica using ethyl acetate–light petroleum (60–80)°C (1:90) as eluent to give a colourless solid of **8** (464 mg, 49%), mp 85–86 °C (Found: C, 58.5; H, 6.1. $C_{24}H_{28}Br_2O$ requires C, 58.6; H, 5.7%); λ_{max}/nm 258 (ε/dm^3 mol^{-1} cm^{-1} 33913) and 301 (32272); δ_H(400 MHz, $CDCl_3$) 0.92–1.00 (6 H, m, 2 × Me), 1.33–1.43 (4 H, m, 2 × CH_2), 1.44–1.65 (4 H, m, 2 × CH_2), 1.76–1.86 (1 H, m, CH), 3.97 (2 H, d, *J* 5.3 Hz, ArOC*H*$_2$), 4.51 (2 H, s, ArC*H*$_2$), 4.72 (2 H, s, ArC*H*$_2$), 6.96 (1 H, s, ArH), 7.34–7.41 (3 H, m, Ar′H), 7.53 (1 H, s, ArH) and 7.55–7.59 (2 H, m, Ar′H); δ_C(125 MHz, $CDCl_3$) 11.2, 14.1, 23.0, 24.0, 27.5, 29.1, 30.6, 31.9, 39.5, 70.6, 86.0 (C≡C), 94.0 (C≡C), 112.6, 115.1, 123.2, 126.9, 128.35, 128.4, 131.5, 134.6, 141.2 and 157.2; *m*/*z* [CI(NH_3)] 491, 493 and 495 (MH^+).

1,4-Bis[ethoxy(thiocarbonyl)thiomethyl]-2-(2′-ethylhexyloxy)-5-(phenylethynyl)benzene 9

A mixture of **8** (341 mg, 0.692 mmol), tetra(*n*-butyl)ammonium bromide (63 mg, 0.194 mmol) and potassium *O*-ethylxanthate (277 mg, 1.73 mmol) in dry dichloromethane (8 cm^3) was stirred at room temperature under argon for 18 h. The reaction mixture was passed through a plug of silica gel using dichloromethane as eluent and the filtrate was collected and the solvent completely removed to give a pale yellow oil (427 mg). The residue was purified by column and chromatotron chromatography over silica using ethyl acetate–light petroleum (1 : 90 and 0 : 1 respectively) to give a colourless oil of **9** (381 mg, 96%) (Found: C, 62.6; H, 6.6. $C_{30}H_{38}O_3S_4$ requires C, 62.7; H, 6.7%); ν_{max}/cm^{-1} (neat) 1046 and 1211; λ_{max}/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 57942), 298(sh) (52722) and 318(sh) (34452); δ_H(500 MHz, $CDCl_3$) 0.93–0.99 (6 H, m, 2 × Me), 1.32–1.38 (4 H, m, 2 × CH_2), 1.41–1.57 (10 H, m, 2 × OCH_2CH_3 and 2 × CH_2), 1.73–1.80 (1 H, m, CH), 3.91 (2 H, d, *J* 5.4 Hz, $ArOCH_2$), 4.35 (2 H, s, $ArCH_2$), 4.61 (2 H, s, $ArCH_2$), 4.65–4.70 (4 H, m, 2 × OCH_2CH_3), 7.00 (1 H, s, ArH), 7.33–7.38 (3 H, m, Ar′H), 7.51–7.53 (2 H, m, Ar′H) and 7.55 (1 H, s, ArH); δ_C(125 MHz, $CDCl_3$) 11.2, 13.8, 14.1, 23.0, 24.0, 29.1, 30.6, 34.9, 39.4, 70.0, 70.1, 70.5, 87.0 ($C{\equiv}C$), 93.8 ($C{\equiv}C$), 112.3, 114.8, 123.3, 124.3, 128.2, 128.3, 131.4, 134.1, 139.1, 157.0, 214.3 (C=S) and 214.5 (C=S); *m/z* (HRMS) found: 574.1721; $C_{30}H_{38}O_3S_4$ requires 574.1703.

Poly([2-(2′-ethylhexyloxy)-5-(phenylethynyl)-1,4-phenylene]{1-[ethoxy(thiocarbonyl)thio]ethylene}) 12

A solution of potassium *tert*-butoxide in tetrahydrofuran (0.19 M, 21 mg, 0.19 mmol, 1.0 cm^3) was added to a solution of **9** in tetrahydrofuran (0.13 M, 118 mg, 0.21 mmol, 1.6 cm^3) which had been cooled with an ice-bath under argon. The reaction mixture was stirred for 1 h with ice-bath cooling and then poured into a solution of methanol (3 cm^3) and water (0.3 cm^3). The mixture was then centrifuged at 4500 rpm for 10 min. The supernatant was removed and the precipitate was dissolved in tetrahydrofuran (3.5 cm^3) and then poured into propan-2-ol (3 cm^3). The mixture was then centrifuged at 4500 rpm for 10 min to give a yellow precipitate of **12** (*ca.* 56 mg, *ca.* 60%) which was dissolved in tetrahydrofuran (3.5 cm^3), ν_{max}(film on KBr disc)/cm^{-1} 1048, 1237 and 2209 ($C{\equiv}C$); δ_H(400 MHz, $CDCl_3$) 0.80–1.00 (6 H, br s, 2 × Me), 1.08–1.60 (11 H, br, 4 × CH_2 and OCH_2CH_3), 1.68–1.83 (1 H, br m, CH), 3.00–3.40 (2 H, br m, $ArCH_2$), 3.70–3.92 (2 H, br m, $ArOCH_2$), 4.20–4.47 (2H, br m, OCH_2Me), 5.62 (1 H, br s, ArCH), 6.80–6.95 (1 H, br, ArH) and 7.20–7.50 (6 H, br, ArH and Ar′H); GPC (0.26 mg cm^{-3}, 23.8 °C), $M_n = 4.0 \times 10^5$, $M_w = 6.8 \times 10^5$, polydispersity index = 1.7 and $M_n = 2.1 \times 10^5$, $M_w = 3.3 \times 10^5$, polydispersity index = 1.6 after equilibration; thermogravimetric analysis: 229 °C (weight loss: 23%; expected: 27%).

Poly[2-(2′-ethylhexyloxy)-5-(phenylethynyl)-1,4-phenylenevinylene] 13

Method 1. Thin films of **10** were heated at 213 °C at 0.01 mmHg for 15 h to give **13**; ν_{max} (film on KBr disc)/cm^{-1} 861, 964, 2204 and 3058; λ_{max}(thin film)/nm 297 and 470.

Method 2. Thin films of **11** were heated at 211 °C at 0.01 mmHg for 15.5 h to give **13**; ν_{max} (film on KBr disc)/cm^{-1} 861, 964, 2206 and 3058; λ_{max}(thin film)/nm 290 and 470.

Method 3. Thin films of **12** were heated at 213 °C at $<$0.01 mmHg for 15 h to give **13**; ν_{max} (film on KBr disc)/cm^{-1} 863, 967, 2207 and 3054; λ_{max}(thin film)/nm 301 and 422.

Acknowledgements

S.-C.L. is a Swire Scholar and holds an Overseas Research Student Award. I.D.W.S. is a Royal Society University Research Fellow. We thank Corning Cables for provision of a studentship (A.K.S.) and Dr M. G. Rüther for helpful discussions and carrying out the thermogravimetric analyses. We also thank Dr C. D. Bain and S. A. Haydock for carrying out the infrared analysis of the spin-coated **13** prepared from **12**.

References

1 (*a*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539; (*b*) A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem. Int. Ed.*, 1998, **37**, 402 and references therein; (*c*) P. L. Burn and I. D. W. Samuel, *Mater. Today*, 1998, **1**, 3; (*d*) J. L. Segura, *Acta Polym.*, 1998, **49**, 319.

2 P. L. Burn, D. D. C. Bradley, R. H. Friend, D. A. Halliday, A. B. Holmes, R. W. Jackson and A. Kraft, *J. Chem. Soc., Perkin. Trans. 1*, 1992, 3225 and references therein; G. J. Lee, D. Kim, J. I. Lee, H. K. Shim, Y. W. Kim and J. C. Jo, *Jpn. J. Appl. Phys.*, 1996, **35**, 114; W. B. Liang, R. W. Lenz and F. E. Karasz, *J. Polym. Sci: Part A Polym. Chem.*, 1990, **28**, 2867; Y. Liu, P. M. Lahti and F. La, *Polymer*, 1998, **39**, 5241; K. L. Brandon, P. G. Bentley, D. D. C. Bradley and D. A. Dunmur, *Synth. Met.*, 1997, **91**, 305; S. A. Chen and E. C. Chang, *Macromolecules*, 1998, **31**, 4899; B. J. Schwartz, F. Hide, M. R. Andersson and A. J. Heeger, *Synth. Met.*, 1997, **84**, 663; E. G. J. Staring, R. C. J. E. Demandt, D. Braun, G. L. J. Rikken and Y. A. R. R. Kessner, *Synth. Met.*, 1995, **71**, 2179; P. L. Burn, A. W. Grice, A. Tajbakhsh, D. D. C. Bradley and A. C. Thomas, *Adv. Mater.*, 1997, **9**, 1171.

3 R. K. McCoy, F. E. Karasz, A. Sarker and P. M. Lahti, *Chem. Mater.*, 1991, **3**, 941; D. P. Norwood, M. Benmouna and W. F. Reed, *Macromolecules*, 1996, **29**, 4293; G. J. Sarnecki, R. H. Friend, A. B. Holmes and S. C. Moratti, *Synth. Met.*, 1995, **69**, 545; R. M. Gurge, A. M. Sarker, P. M. Lahti, B. Hu and F. E. Karasz, *Macromolecules*, 1997, **30**, 8286; I. N. Kang, D. H. Hwang and H. K. Shim, *Synth Met.*, 1995, **69**, 547; J. I. Lee, J. Y. Han, H. K. Shim, S. C. Jeoung and D. Kim, *Synth. Met.*, 1997, **84**, 261.

4 H. A. Reisch and U. Scherf, *Macromol. Chem. Phys.*, 1999, **200**, 552; J. I. Jin, C. K. Park and H. K. Shim, *J. Polym. Sci: Part A*, 1991, **29**, 93.

5 H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H. Schenk, R. Demandt and H. Schoo, *Adv. Mater.*, 1998, **10**, 1340; B. R. Hsieh, H. Antoniadis, D. C. Bland and W. A. Feld, *Adv. Mater.*, 1995, **7**, 36.

6 H. Park, Y. S. Choi and Y. W. Park, *Synth. Met.*, 1997, **84**, 965; J. Gordon, T. J. Sheldon, D. D. C. Bradley and P. L. Burn, *J. Mater. Chem.*, 1996, **6**, 1253; J. I. Jin, Y. H. Lee, B. K. Nam and M. Y. Lee, *Chem. Mater.*, 1995, **7**, 1897; J. I. Jin, Y. H. Lee and B. K. Nam, *Polymer*, 1995, **36**, 193; J. I. Jin, Y. H. Lee and B. K. Nam, *Macromolecules*, 1994, **27**, 5239.

7 L. S. Swanson and J. Shinar, *Synth. Met.*, 1993, **55–57**, 1; R. Fiesel and U. Scherf, *Macromol. Rapid Commun.*, 1998, **19**, 427.

8 S.-C. Lo, A. K. Sheridan, I. D. W. Samuel and P. L. Burn, *J. Mater. Chem.*, 1999, **9**, 2165.

9 D. W. J. McCallien, A. C. Thomas and P. L. Burn, *J. Mater. Chem.*, 1999, **9**, 847; F. H. Boardman, A. W. Grice, M. G. Rüther, T. J. Sheldon, D. D. C. Bradley and P. L. Burn, *Macromolecules*, 1999, **32**, 111.

10 S. Son, A. Dodabalapur, A. J. Lovinger and M. E. Galvin, *Science*, 1995, **269**, 376.

11 P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Nature*, 1992, **356**, 47.

12 I. D. W. Samuel, G. Rumbles and C. J. Collison, *Phys. Rev. B*, 1995, **52**, 11573.

13 I. D. W. Samuel, G. Rumbles and R. H. Friend, *Luminescence efficiency and time-dependence: insights into the nature of the emitting species in conjugated polymers. Primary photoexcitations in conjugated polymers: molecular exciton versus semiconductor band model*, ed. N. S. Sariciftci, World Scientific, Singapore, 1997, 140.

14 N. C. Greenham, I. D. W. Samuel, R. T. Phillips, Y. A. R. R. Kessner, S. C. Morratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, 241.

15 R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, **28**, 3313.

Paper a904274a