The synthesis of an electronically asymmetric substituted poly(arylenevinylene); poly{2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]-1,4-phenylenevinylene}

John Gordon,[a] Timothy J. Sheldon,[a] Donal D. C. Bradley[b] and Paul L. Burn*[a]

[a]*The Dyson Perrins Laboratory, South Parks Road, Oxford, UK OX1 3QY*

[b]*Department of Physics & Centre for Molecular Materials, University of Sheffield, Hounsfield Road, Sheffield, UK S3 7RH*

We have found that by the inclusion of a conjugated spacer it is possible to synthesise a poly(1,4-phenylenevinylene) derivative with an electron-withdrawing group attached directly from the substituted monomer. We describe a route for the synthesis of an electronically asymmetric styryl-derivatised poly(1,4-phenylenevinylene). The preparation was achieved in two steps from the nitrostyryl-substituted arylenedimethylene bisbromo monomer **13**. In the first step, base-induced polymerisation of **13** afforded the soluble and processible precursor polymer **14**. The precursor polymer **14** could then be converted in the second step to the insoluble and unprocessible conjugated polymer **15** by thermal treatment in the solid state.

Poly(arylenevinylene)s have been increasingly investigated for use as the electroactive components in opto-electronic applications such as light-emitting diodes (LEDs)[1,2] and non-linear optics (NLO).[3,4,5] Due to their rigid rod character, simple conjugated polymers are generally not soluble in common solvents, and this leads to difficulties both in their synthesis and processing. This problem has been overcome by two main methods, the first being the preparation of a soluble precursor polymer which can be processed into the required form before conversion in the solid state into an insoluble conjugated polymer.[6] An example of this route is illustrated by the synthesis of poly(1,4-phenylenevinylene) (PPV) from poly{1,4-phenylene[1-(tetrahydrothiophen-1-io)ethylene chloride]}.[6] The second approach involves the attachment of lipophilic side groups to the polymer backbone which solubilise the polymer in the conjugated state.[7] Of the two routes the former is preferred as it allows the facile development of more complex multilayer devices. The synthetic procedures for synthesising PPVs with electron-donating groups attached to the phenylene moiety are well understood.[6] However, the synthesis of PPVs and copolymers of PPVs with electron-withdrawing groups or a combination of the two types of groups attached to the polymer backbone, and in particular the phenylene moiety, has proved more difficult to achieve.[8,9,10] Such polymers are of particular interest for use in LEDs[10,11] and in the latter case second-order [$\chi^{(2)}$] NLO.[3] We present in this paper a route which enables the facile preparation of derivatised poly(1,4-phenylenevinylene)s containing electron-withdrawing groups and illustrate it by the preparation of the new conjugated polymer, poly[2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]-1,4-phenylenevinylene] **15**.

Results and Discussion

Monomer synthesis

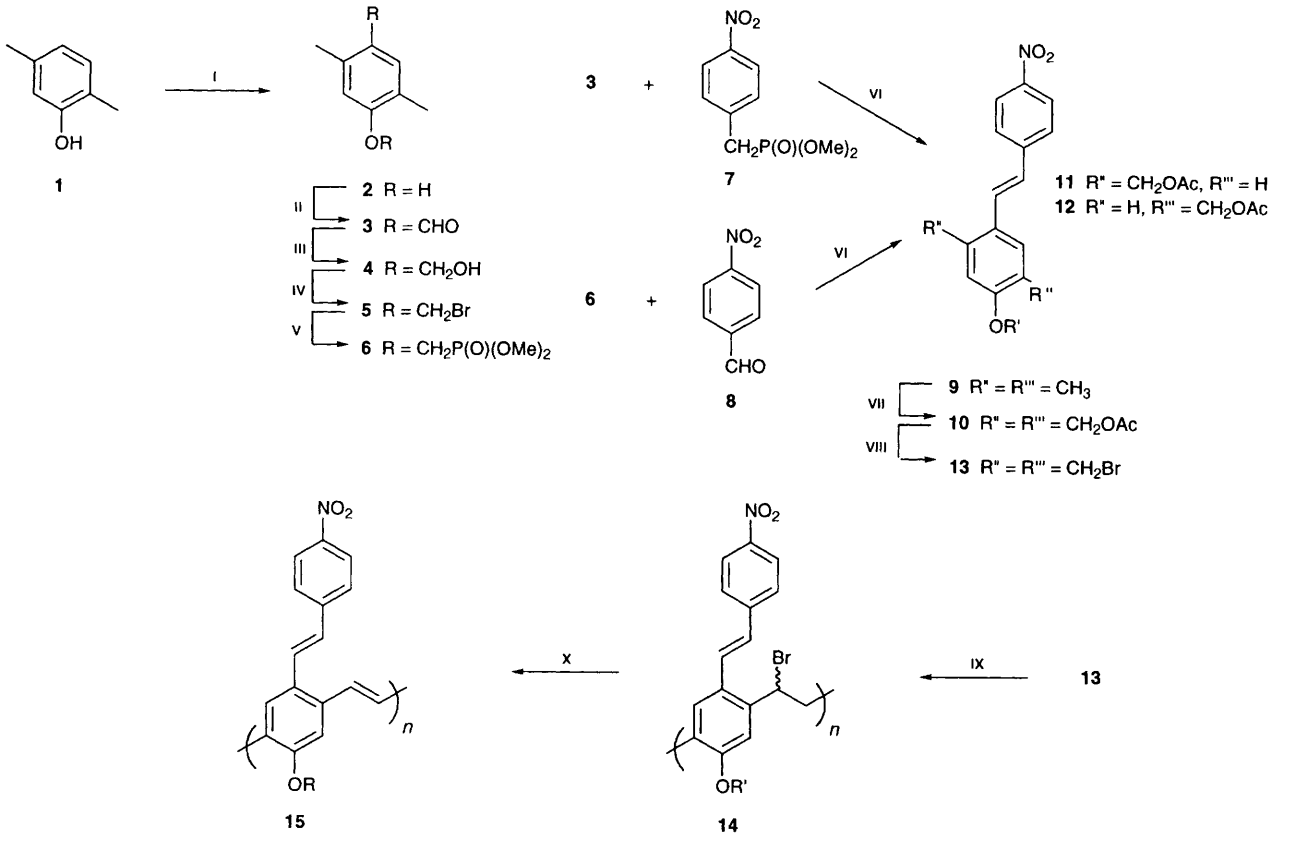
Poly(arylenevinylene) precursor polymers are generally synthesised by base-induced polymerisation of monomers containing either arylenedimethylene bissulfonium salts[6] or arylenedimethylene bishalogen moieties.[12,13,14] However, when strong electron-withdrawing groups are attached to the phenylene group this route generally fails to give good polymers.[8,9] To avoid this our strategy was to link electronically the electron-withdrawing group to the phenylene group *via* a conjugated unit. For this investigation we chose the styryl group to be the link, thus making the monomer the substituted stilbene **13**. Due to the lipophilic nature of the monomer we decided to utilise the arylenedimethylene bishalogen route for the preparation of **14**. We considered that following the arylenedimethylene bissulfonium route would give rise to solubility problems during the polymerisation, purification and processing steps as such problems were encountered in recent syntheses of poly{2-[(*E*)-styryl]-1,4-phenylenevinylene} and poly{2-methoxy-5-[(*E*)-styryl]-1,4-phenylenevinylene}.[15]

Our synthetic scheme (Scheme 1) was designed to allow the facile introduction of different functional groups onto the polymer. For example, by changing the alkoxy R′ group we would be able to vary the solubility and thermal properties of the polymer. In this investigation we chose R′ to be the 2-ethylhexyl group so as to impart solubility to the intermediates on the pathway to **15**.

The first target in the synthesis was the preparation of the stilbene **9**. It was envisaged that synthesis of **9** could be achieved by two different Horner–Emmons reactions, that is, by coupling phosphonate **6** with 4-nitrobenzaldehyde **8** or alternatively, phosphonate **7** with aldehyde **3**. Conceptually the former route is more elegant as inexpensive *para*-substituted benzaldehydes containing a number of functional groups are readily available and hence coupling with **6** would give rapid access to a number of different chromophores.

The first step in the synthesis of stilbene **9** was to couple commercially available 2,5-dimethylphenol **1** and 1-bromo-2-ethylhexane to give **2**. This was achieved in 61% yield by reacting the sodium salt of **1** with 1-bromo-2-ethylhexane in *N*,*N*-dimethylformamide. Attempts to introduce the required chloromethane group for the formation of phosphonate **6** by chloromethylating **2** were unsuccessful. This required us to use a more circuitous route which involved the elaboration of aldehyde **3**. Aldehyde **3** was easily prepared from **2** in yields of up to 90% by the Vilsmeier reaction. It should be noted that the Vilsmeier reaction was exothermic and so great care had to be taken when heating the reaction mixture. The aldehyde **3** was reduced to the primary alcohol **4** in a 93% isolated yield by treatment with sodium borohydride at room temperature. Bromination of **4** was achieved with phosphorus tribromide in two hours to give **5** in an 82% isolated yield. The phosphonate **6** was finally prepared by the Arbuzov reaction in an 85% yield.

Coupling of the phosphonate **6** with commercially available 4-nitrobenzaldehyde **8** to produce the (*E*)-stilbene **9** proved unproductive and only low yields (22%) containing variable mixtures of the (*E*) and (*Z*) isomers of **9** were obtained. The



Scheme 1 *Reagents and Conditions* i, NaH, DMF, 1-bromo-2-ethylhexane (R'Br), 0 °C to room temp., ii, $POCl_3$, DMF, Δ, iii, $NaBH_4$, EtOH, room temp., iv, PBr_3, CH_2Cl_2, room temp., v, $P(OMe)_3$, Δ, vi, NaH, DMF, 0 °C, room temp., vii, NBS, AIBN, CCl_4, Δ then NaOAc, CH_3CO_2H, Δ, viii, HBr (47%), 1,4-dioxane, Δ, ix, $KOBu^t$, THF, x, 200 °C, vacuum

poor yield and lack of stereoselectivity made it necessary to follow the alternative pathway to **9** and couple **7** with **3** 4-Nitrobenzyldimethylphosphonate **7** was prepared from the commercially available 4-nitrobenzyl bromide in an 83% yield by the Arbusov reaction Coupling the anion of **7** with **3** gave after 36 hours exclusively the (*E*) isomer of **9** in an 81% yield

All that remained for us to do was to activate the two methyl groups and form **13** We envisaged that this could be achieved by the radical bromination of the benzylic carbons with *N*-bromosuccinimide However, we found that when **9** was reacted with 2 1 equivalents of *N*-bromosuccinimide for four hours a mixture of brominated compounds which were inseparable by chromatography was formed This meant we had to develop a reaction sequence which would allow us to isolate pure **13** We found that the crude mixture of bromides could be acetylated by treatment with anhydrous sodium acetate in glacial acetic acid The bisacetylated **10** could then be easily separated by column chromatography over silica in a 32% yield from the other components, the main one being an inseparable mixture of the two monoacetylated compounds **11** and **12** which were isolated in a combined yield of 37% Conversion of **10** to **13** was finally achieved in a yield of 76% by treatment of **10** with hydrobromic acid in refluxing 1,4-dioxane for two hours

Polymer synthesis

Previous investigations into the polymerisation of arylenedimethylene bishalogen compounds have shown that by using an excess of base it is possible to go directly to the conjugated polymer [16] However, if only one equivalent of the base is used then it is possible to isolate the precursor polymer [12,13] With this in mind we carried out the base-catalysed polymerisations with less than one equivalent of base In a typical polymerisation, 0 9 equivalents of a 0 25 M solution of potassium *tert*-butoxide in tetrahydrofuran was added to a 0 25 M solution of **13** in tetrahydrofuran The reaction mixture was then stirred at room temperature for one hour before being terminated The crucial factor which determined the success of the polymerisation was the concentration of the base and **13** If the concentrations were too low then very little polymer formed, whilst if the concentrations of the two components were too high then an insoluble gel formed We found that the best method of purifying **14** was to carry out a series of reprecipitations which removed not only the inorganic salts but also low molecular weight materials and remaining monomer Gel permeation chromatography (GPC) analysis (against polystyrene standards) of **14** indicated that we had formed a polymer with a M_w of 3.5×10^5 and a polydispersity 8 1 **14** was found to be soluble in polar aprotic solvents such as tetrahydrofuran, chloroform and dichloromethane and good quality thin films of **14** could be prepared by spin-coating **14** dissolved in tetrahydrofuran Thermogravimetry (TG) of **14** showed that there was a thermal transition at approximately 200–230 °C which we attributed to the elimination of hydrogen bromide This was confirmed by analysis of the emitted gas from the TG by GC–MS, which showed that at this temperature the molecule that was emitted had a molecular weight of 80 In addition, differential scanning calorimetry showed that **14** had a glass transition temperature in the range 125–128 °C The presence of a glass transition temperature is important for our interest in investigating **15** for $\chi^{(2)}$ NLO effects, which requires the chromophores to be aligned in the film We investigated the conversion of **14** to **15** by preparing three film samples of **14**, a sample which was spin-coated onto a glass slide for UV–VIS analysis, a film deposited onto a KBr disc for infrared analysis and a free standing film for microanalysis Utilising the data from the TG, **14** was heated for four hours at 200 °C under vacuum and during this process the films went rapidly red Comparison of the infrared spectra of **14** and **15**

showed that there was an increase in oscillator strength at 962 cm^{-1} which is attributed to the C–H out-of-plane bend of a *trans* vinylene group indicating that elimination had occurred and that **15** was being formed. The UV–VIS absorption spectrum of **14** and **15** are shown in Fig. 1. The UV–VIS spectrum of **14** has an absorption maxima at 374 nm, which is the same wavelength as that observed for **13** and is due to the stilbene chromophore. After thermal conversion to **15** the absorption edge moves to longer wavelengths and the maximum is at 360 nm. This absorption band is very broad compared to the UV–VIS spectra normally observed for PPVs. Broadness in the UV–VIS absorption spectra of conjugated polymers is normally due to the presence of a range of 'effective' conjugation lengths which can be caused by chemical and/or conformational defects. To discount the former possibility we microanalysed the sample of film converted at the same time as the sample used for the UV–VIS analysis. The results showed that within the allowed experimental error the carbon, hydrogen and nitrogen content were as expected for the fully conjugated material, indicating that the reaction had gone to completion. Therefore, we consider that the broad UV–VIS absorption of **15** is due to overlap of the conjugated backbone and stilbene unit spectra as well as disruption to the planarity of the chromphores caused by steric interactions. Twisting the conjugated units out of planarity causes a decrease in π-orbital overlap and a blue shift in UV–VIS absorption spectra. This type of steric interaction has been observed in some other 2,5-substituted PPVs. For example, the UV–VIS absorption spectrum of poly(2,5-dimethyl-1,4-phenylenevinylene) is blue shifted when compared to the absorption of PPV and this is thought to be due to a decrease in planarity of the polymer caused by the allylic strain originating from the aromatic methyl groups.[6] In the case of **15** the twisting out of planarity of both the conjugated backbone and the stilbene units is caused by steric interactions between the vinylic protons of the stilbene units with the vinylic protons of the polymer backbone. The evidence for this is strengthened by the fact that the absorption maximum of the stilbene chromophore is at 360 nm, which is blue shifted when compared with the spectrum of the precursor polymer.

Experimental

Measurements

NMR spectra were recorded on a Bruker 500 MHz spectrometer; *J* values are given in Hz. ^{13}C NMR spectra were fully decoupled. IR spectra were recorded on a Perkin-Elmer 781 IR spectrometer. All spectra were recorded as solutions in distilled chloroform unless otherwise stated. UV–VIS spectra were recorded on Perkin-Elmer UV–VIS Spectrometers (Lambda 2 or Lambda 14P) and unless otherwise stated, all spectra were recorded as solutions in distilled chloroform. Mass spectra were recorded on either a VG 20-250 mass spectrometer or a VG Mass Lab Trio 1 GC-mass 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 Mrs V. Lamburn in the department. Gel permeation chromatography separations were carried out with a Polymer Laboratories Plgel 5 μm MIXED-D column (300 mm length) calibrated with polystyrene narrow standards (mass range 580–400 000) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran solvent was pumped at 1 cm^3 min^{-1} at 28 °C and the UV detector was set at 265 nm. Spin-coated samples were prepared by covering a substrate with a solution of the precursor polymer and spinning this at 2000 revolutions per min for 60 s on a Dynapert PRS 14E spinner for photoresists, the solvent being allowed to evaporate under ambient conditions.

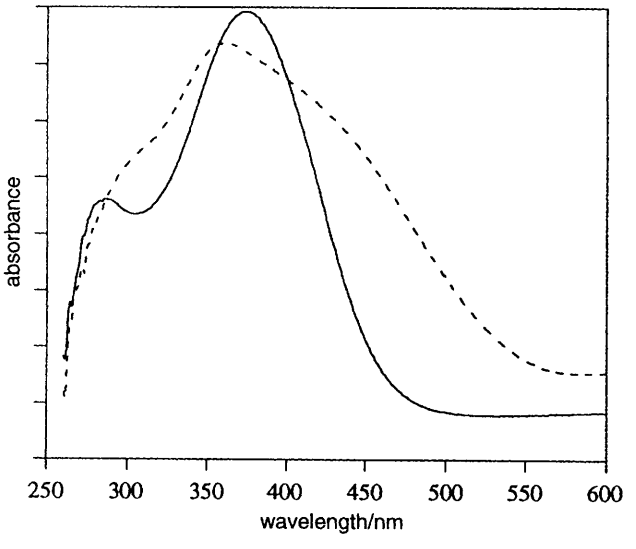


Fig. 1 UV–VIS absorption spectra of **14** (—) and **15** (– – –)

1,4-Dimethyl-2-(2′-ethylhexyloxy)benzene 2

A mixture of 2,5-dimethylphenol **1** (29.2 g, 0.260 mol) in dry *N*,*N*-dimethylformamide (600 cm^3) was cooled to 0 °C under nitrogen. Sodium hydride (60%; 14.6 g, 0.364 mol) was added slowly and the mixture was stirred at 0 °C for 3 h during which time a white precipitate formed. A solution of 2-ethylhexylbromide (50.0 g, 0.260 mol) in dry *N*,*N*-dimethylformamide (100 cm^3) was added dropwise to the reaction mixture and the mixture was stirred for 16 h at room temperature. Diethyl ether (600 cm^3) and water (600 cm^3) were added to the resultant solution and the organic layer was separated. The organic layer was washed with water (8×400 cm^3), sodium hydroxide solution (10%; 2×250 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed. The residue was purified by distillation to yield a colourless oil, 1,4-dimethyl-2-(2′-ethylhexyloxy)benzene **2** (36.6 g, 61%), bp 118 °C at 0.5 mmHg; λ_{max}/nm 277 (ε/dm^3 mol^{-1} cm^{-1} 1518) and 282 (1484); δ_H(500 MHz; $CDCl_3$) 0.95 (6 H, m, $2 \times CH_3$), 1.35 (4 H, m, $2 \times CH_2$), 1.44–1.58 (4 H, m, $2 \times CH_2$), 1.76 (1 H, m, CH), 2.20 (3 H, s, $ArCH_3$), 2.34 (3 H, s, $ArCH_3$), 3.86 (2 H, d, *J* 5, OCH_2), 6.67 (2 H, m, 3-H and 5-H) and 7.02 (1 H, d, *J* 7, 6-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 15.8, 21.4, 23.1, 24.1, 29.1, 30.7, 39.6, 70.1, 111.8, 120.4, 123.7, 130.2, 136.4, and 157.3; *m*/*z* [CI(NH_3)] 234 (M^+) and 235 (MH^+).

2,5-Dimethyl-4-(2′-ethylhexyloxy)benzaldehyde 3

Phosphoryl chloride (2.0 cm^3, 22 mmol) was added slowly to dry *N*,*N*-dimethylformamide (10 cm^3) which had been cooled to 0 °C under nitrogen. During the addition the temperature of the reaction mixture was kept below 5 °C, and then the reaction mixture was stirred at room temperature for 0.5 h. 1,4-Dimethyl-2-(2′-ethylhexyloxy)benzene **2** (1.0 g, 4.3 mmol) was added slowly and the mixture was heated *carefully* to reflux and then held at reflux for 2 h. After cooling, the reaction mixture was poured onto ice–water (100 cm^3) and the aqueous layer was extracted with ether (3×75 cm^3). The organic layers were combined, washed with water (5×100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed to yield a yellow oil. The residue was chromatographed on silica gel using dichloromethane–light petroleum (3:2) as eluent to give 2,5-dimethyl-4-(2′-ethylhexyloxy)-benzaldehyde **3** (0.94 g, 90%). A sample for analysis was distilled, bp 212 °C at 0.5 mmHg (Found: C, 77.6; H, 10.1. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); ν_{max}/cm^{-1} 1679 (C=O); λ_{max}/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 15401); δ_H(500 MHz; $CDCl_3$) 0.94 (6 H, m, $2 \times CH_3$), 1.34 (4 H, m, $2 \times CH_2$), 1.50

(4 H, m, $2\times CH_2$), 1.77 (1 H, m, CH), 2.23 (3 H, s, $ArCH_3$), 2.65 (3 H, s, $ArCH_3$), 3.94 (2 H, d, *J* 5.5, OCH_2), 6.65 (1 H, s, 3-H), 7.59 (1 H, s, 6-H) and 10.12 (1 H, s, CHO); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 15.6, 19.5, 23.0, 24.0, 29.1, 30.6, 39.4, 70.5, 113.2, 124.9, 126.8, 134.0, 141.1, 161.7 and 191.2; *m/z* [CI(NH_3)] 263 (MH^+).

2,5-Dimethyl-4-(2′-ethylhexyloxy)benzyl alcohol 4

Sodium borohydride (5.0 g, 132 mmol) was added to a solution of 2,5-dimethyl-4-(2′-ethylhexyloxy)benzaldehyde **3** (4.5 g, 17 mmol) in ethanol (30 cm^3) and the mixture was stirred for 2 h at room temperature. The solvent was completely removed and the residue redissolved in ether (150 cm^3). Hydrochloric acid (1 M; 80 cm^3) was added and the organic layer was separated, washed with water (4×100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed to yield a yellow oil. The oil was redissolved in dichloromethane (150 cm^3) and filtered through a plug of silica. The solvent was completely removed to yield a light yellow oil, 2,5-dimethyl-4-(2′-ethylhexyloxy)benzylalcohol **4** (4.2 g, 93%). A sample for analysis was distilled, bp 250 °C at 0.3 mmHg (Found: C, 77.2; H, 10.8. $C_{17}H_{28}O_2$ requires C, 77.2; H, 10.7%); ν_{max}/cm^{-1} 3608 (OH); λ_{max}/nm 279 (ε/dm^3 mol^{-1} cm^{-1} 1838) and 285 (1838); δ_H(500 MHz; $CDCl_3$) 0.95 (6 H, m, $2\times CH_3$), 1.35 (4 H, m, $2\times CH_3$), 1.50 (5 H, m, $2\times CH_2$ and OH), 1.75 (1 H, m, CH), 2.20 (3 H, s, $ArCH_3$), 2.37 (3 H, s, $ArCH_3$), 3.86 (2 H, d, *J* 5, OCH_2), 4.61 (2 H, s, CH_2OH), 6.67 (1 H, s, 3-H) and 7.09 (1 H, s, 6-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 15.6, 18.7, 23.0, 24.1, 29.1, 30.7, 39.5, 63.3, 70.2, 113.1, 124.1, 130.0, 130.9, 134.9 and 157.0; *m/z* [CI(NH_3)] 265 (MH^+).

2,5-Dimethyl-4-(2′-ethylhexyloxy)benzyl bromide 5

A solution of 2,5-dimethyl-4-(2′-ethylhexyloxy)benzyl alcohol **4** (400 mg, 1.52 mmol) in dry dichloromethane (15 cm^3) was cooled to 0 °C under nitrogen. Phosphorus tribromide (1.5 cm^3, 17 mmol) was slowly added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was poured onto crushed ice (50 g) and dichloromethane (50 cm^3) was added. The organic layer was separated and washed with water (10×100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed to yield an oil of 2,5-dimethyl-4-(2′-ethylhexyloxy)benzyl bromide **5** (404 mg, 82%). A sample for analysis was distilled, bp 244 °C at 0.3 mmHg (Found: C, 62.6; H, 8.5. $C_{17}H_{27}OBr$ requires C, 62.4; H, 8.3%); λ_{max}/nm 262 (ε/dm^3 mol^{-1} cm^{-1} 9684); δ_H(500 MHz; $CDCl_3$) 0.94 (6 H, m, $2\times CH_3$), 1.35 (4 H, m, $2\times CH_2$), 1.49 (4 H, m, $2\times CH_2$), 1.75 (1 H, m, CH), 2.18 (3 H, s, $ArCH_3$), 2.40 (3 H, s, $ArCH_3$), 3.86 (2 H, d, *J* 5.5, OCH_2), 4.54 (2 H, s, CH_2Br), 6.64 (1 H, s, 3-H) and 7.09 (1 H, s, 6-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 15.6, 18.9, 23.0, 24.1, 29.1, 30.7, 33.5, 39.5, 70.2, 113.0, 124.7, 126.8, 132.3, 136.0 and 157.8; *m/z* (EI) 326 and 328 (M^+).

2,5-Dimethyl-4-(2′-ethylhexyloxy)benzyldimethylphosphonate 6

A solution of 2,5-dimethyl-4-(2′-ethylhexyloxy)benzyl bromide **5** (2.13 g, 6.51 mmol) in trimethylphosphite (8.0 cm^3, 68 mmol) was heated at 100 °C for 3 h. After cooling, the reaction mixture was added to ether (150 cm^3) and the organic layer was washed with water (3×100 cm^3), brine (100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed to yield a yellow oil. The residue was chromatographed on silica gel using dichloromethane–methanol (24:1) as eluent to give a light yellow oil. This was further purified by Kugelrohr distillation and the fraction, bp 250 °C at 0.3 mmHg, collected to yield 2,5-dimethyl-4-(2′-ethylhexyloxy)benzyldimethylphosphonate **6** (1.98 g, 85%) (Found: C, 64.3; H, 9.5. $C_{19}H_{33}PO_4$ requires C, 64.0; H, 9.3%); ν_{max}/cm^{-1} 1038 ($POCH_3$), 1061 ($POCH_3$) and 1245 (P=O); λ_{max}/nm 280 (ε/dm^3 mol^{-1} cm^{-1} 2056) and 287 (2056); δ_H(500 MHz; $CDCl_3$) 0.94 (6 H, m, $2\times CH_3$), 1.34 (4 H, m, $2\times CH_2$), 1.48 (4 H, m, $2\times CH_2$), 1.73 (1 H, m, CH), 2.17 (3 H, s, $ArCH_3$), 2.33 (3 H, d, *J* 1.5, $ArCH_3$), 3.09 (2 H, d, *J* 21, CH_2P), 3.66 (6 H, d, *J* 11, $2\times OCH_3$), 3.82 (2 H, d, *J* 5, OCH_2), 6.62 (1 H, s, 3-H) and 7.00 (1 H, d, *J* 2.5, 6-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 15.7, 19.9, 23.0, 24.1, 29.1, 29 (d, *J* 40, CH_2P), 30.7, 39.5, 52.7 (d, *J* 6, $POCH_3$), 70.1, 112 120.3 [d, *J* 9, C(1)], 124.4, 132.5 [d, *J* 4, C(6)], 135.0 a 156.4; *m/z* [CI(NH_3)] 357 (MH^+), 374 (MNH_4^+).

4-Nitrobenzyldimethylphosphonate 7

A solution of 4-nitrobenzyl bromide (26.6 g, 0.123 mol) trimethylphosphite (60.0 cm^3, 0.509 mol) was heated at 100 under nitrogen for 17 h. After the mixture had cooled, it w added to ethyl acetate (500 cm^3) and the organic layer w washed with brine (4×400 cm^3), dried over anhydrous sodiu sulfate, filtered and the solvent completely removed to yield yellow solid. The residue was chromatographed on silica g using dichloromethane–methanol (19:1) as eluent to give nitrobenzyldimethylphosphonate **7** (24.9 g, 83%). A sample f analysis was recrystallised from methanol, mp 68 °C (Foun C, 44.35; H, 4.9; N, 5.8. $C_9H_{10}NO_5P$ requires C, 44.1; H, 4 N, 5.7%); ν_{max}/cm^{-1} 1031 ($POCH_3$), 1069 ($POCH_3$), 12 (P=O), 1350 (NO_2) and 1524 (NO_2); λ_{max}/nm 272 (ε/d mol^{-1} cm^{-1} 9854); δ_H(500 MHz; $CDCl_3$) 3.26 (2 H, d, *J* 2 CH_2P), 3.71 (6 H, d, *J* 11, $2\times OCH_3$), 7.48 (2 H, m, 2-H a 6-H) and 8.20 (2 H, AA′BB′, 3-H and 5-H): δ_C(125 MH $CDCl_3$) 33.0 (d, *J* 138, CH_2P), 53.0 (d, *J* 6, $POCH_3$), 12 [C(3) and (C(5)], 130.6 [d, *J* 6, C(2) and C(6)], 139.2 [d, 9, C(1)] and 147.1 [C(4)]; *m/z* [CI(NH_3)] 245 (M^+), 2 (MH^+), 263 (MNH_4^+).

1,4-Dimethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene 9

Method 1. A mixture of 4-nitrobenzyldimethylphosphona **7** (14.5 g, 59.3 mmol) and sodium hydride (60%; 3.3 83 mmol) in dry *N*,*N*-dimethylformamide (300 cm^3) was cool to 0 °C under nitrogen. 2,5-Dimethyl-4-(2′-ethylhexylox benzaldehyde **3** (18.7 g, 71.2 mmol) in dry *N*,*N*-dimethylform mide (100 cm^3) was added dropwise, keeping the temperatu below 3 °C. The reaction mixture was then stirred for 36 h room temperature. The mixture was added to ether (500 cm and the organic layer was washed with water (3×500 cm brine (3×400 cm^3), dried over anhydrous sodium sulfa filtered and the solvent completely removed to yield an oran oil. The residue was chromatographed on silica gel usi dichloromethane–light petroleum (1:4) as eluent to give 1, dimethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene (18.3 g, 81%); mp 56 °C (Found: C, 75.7; H, 7.8; N, 3 $C_{24}H_{31}NO_3$ requires C, 75.6; H, 8.2; N, 3.7%); ν_{max}/cm^{-1} 13 (NO_2), 1508 (NO_2) and 1609 (C=C); λ_{max}/nm 263 (ε/d mol^{-1} cm^{-1} 10718), 289sh (10454) and 395 (2291 δ_H(500 MHz; $CDCl_3$) 0.96 (6 H, m, $2\times CH_3$), 1.36 (4 H, $2\times CH_2$), 1.52 (4 H, m, $2\times CH_2$), 1.78 (1 H, m, CH), 2.25 H, s, $ArCH_3$), 2.45 (3 H, s, $ArCH_3$), 3.89 (2 H, d, *J* 5.5, OCH 6.66 (1 H, s, 3-H), 6.95 (1 H, d, *J* 16, vinyl-H), 7.43 (1 H, s, H), 7.47 (1 H, d, *J* 16, vinyl-H), 7.60 and 8.21 (4 H, AA′BB 2″-H, 3″-H, 5″-H and 6″-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14 15.9, 19.8, 23.0, 24.1, 29.1, 30.7, 39.5, 70.3, 112.8, 124.1, 124 124.9, 126.5, 126.7, 127.7, 130.8, 135.5, 144.8, 146.3 and 158 *m/z* [CI(NH_3)] 381 (M^+), 382 (MH^+).

Method 2. A mixture of 2,5-dimethyl-4-(2′-ethylhexylox benzyldimethylphosphonate **6** (500 mg, 1.40 mmol) a sodium hydride (60%; 78 mg, 2.0 mmol) in dry *N*,*N*-dimethy formamide (20 cm^3) was cooled to 0 °C under nitrogen. Nitrobenzaldehyde **8** (255 mg, 1.69 mmol) in dry *N*,*

dimethylformamide (10 cm^3) was added dropwise, keeping the temperature below 3 °C. The reaction mixture was stirred between 0–5 °C for 30 mins before being stirred at room temperature for 2 h. The mixture was then added to ether (200 cm^3) and the organic layer was washed with water (3 × 100 cm^3), brine (100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed to yield an orange oil. The oil was chromatographed on silica gel using dichloromethane–light petroleum (2:1) as eluent to give an impure residue. The residue was further purified by preparative layer chromatography on silica gel using dichloromethane–light petroleum (4:1) as eluent to give an inseparable mixture of 1,4-dimethyl-2-(2′-ethylhexyloxy)-5-[(*Z*)-4″-nitrostyryl]benzene and **9** (118 mg, 22%).

1,4-Bis(acetoxymethyl)-2-(2′-ethylhexyloxy)-5[(*E*)-4″-nitrostyryl]benzene 10

A solution of 1,4-dimethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl)benzene **9** (100 mg, 0.262 mmol), *N*-bromosuccinimide (99 mg, 0.55 mmol) and AIBN (20 mg, 0.12 mmol) in carbon tetrachloride (15 cm^3) was heated at reflux for 4 h. After the mixture had cooled, the solvent was completely removed. The reaction mixture was redissolved in dichloromethane (100 cm^3), filtered through a plug of silica and the solvent was completely removed to yield a yellow oil (134 mg) containing a mixture of brominated products. A mixture of the yellow oil (134 mg) and anhydrous sodium acetate (89 mg, 1.1 mmol) in glacial acetic acid (10 cm^3) was heated at reflux for 2 h. After cooling, the reaction mixture was poured onto crushed ice (50 g). Water (50 cm^3) and diethyl ether (100 cm^3) were added. The organic layer was separated and washed with water (3 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent completely removed. Preparative layer chromatography on silica gel using dichloromethane–light petroleum (2:1) as eluent yielded two main fractions. The first fraction (R_f 0.58) contained a yellow oil which was an inseparable mixture of 1-acetomethyl-2-(2′-ethylhexyloxy)-4-methyl-5-[(*E*)-4″-nitrostyryl]benzene **12** and 4-acetomethyl-2-(2′-ethylhexyloxy)-1-methyl-5-[(*E*)]-4″-nitrostyryl]benzene **11**, (46 mg, 37%) (Found: C, 70.9; H, 7.5; N, 3.2. $C_{26}H_{33}NO_5$ requires C, 71.05; H, 7.6; N, 3.2%); ν_{max}/cm^{-1} 1343 (NO_2), 1516 (NO_2), 1593 (C=C) and 1735 (C=O); λ_{max}/nm 381 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 24190); δ_H(500 MHz; $CDCl_3$) 0.94 (6 H, m, 2 × CH_3), 1.33 (4 H, m, 2 × CH_2), 1.48 (4 H, m, 2 × CH_2), 1.76 (1 H, m, CH), 2.10 and 2.11 (3 H, s, $COCH_3$), 2.27 and 2.47 (3 H, s, $ArCH_3$), 3.92 (2 H, m, OCH_2), 5.16 and 5.26 (2 H, s, CH_2OAc), 6.74 and 6.86 (1 H, s, 3-H), 6.97 and 6.99 (1 H, d, *J* 16, vinyl-H), 7.45 and 7.50 (1 H, d, *J* 16, vinyl-H), 7.50 and 7.62 (1 H, s, 6-H) and 7.62 and 8.23 (4 H, m, 2″-H, 3″-H, 5″-H and 6″-H); δ_C(125 MHz; $CDCl_3$) 11.15, 11.23, 14.1, 16.2, 20.2, 21.1, 23.0, 23.9, 24.1, 29.1, 30.6, 30.7, 39.4, 39.5, 61.8, 64.2, 70.4, 112.6, 113.3, 122.5, 124.2, 125.6, 126.2, 126.6, 126.7, 127.1, 127.4, 127.7, 128.2, 129.5, 130.2, 132.6, 138.6, 144.3, 144.5, 146.5, 157.8, 158.0, 170.8 and 171.0; *m/z* [DCI(NH_3)] 439 (M^+), 440 (MH^+). The second fraction (R_f 0.28) yielded 1,4-bis(acetoxymethyl)-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene **10** (41 mg, 32%). A sample for analysis was recrystallised from methanol, mp 109–110 °C (Found: C, 67.7; H, 7.0; N, 2.8. $C_{28}H_{35}NO_7$ requires C, 67.6; H, 7.1; N, 2.8%); ν_{max}/cm^{-1} 1343 (NO_2), 1517 (NO_2), 1594 (C=C) and 1736 (C=O); λ_{max}/nm 256 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 8543), 289sh (5845) and 373 (17386); δ_H(500 MHz; $CDCl_3$) 0.95 (6 H, m, 2 × CH_3), 1.34 (4 H, m, 2 × CH_2), 1.49 (4 H, m, 2 × CH_2), 1.77 (1 H, m, CH), 2.11 (3 H, s, $COCH_3$), 2.12 (3 H, s, $COCH_3$), 3.95 (2 H, m, OCH_2), 5.19 (2 H, s, CH_2OAc), 5.28 (2 H, s, CH_2OAc), 6.94 (1 H, s, 3-H), 7.00 (1 H, d, *J* 16, vinyl-H), 7.49 (1 H, d, *J* 16, vinyl-H), 7.67 (1 H, s, 6-H), 7.63 and 8.23 (4 H, AA′BB′, 2″-H, 3″-H, 5″-H and 6″-H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.0, 21.0, 23.0, 23.9, 29.1, 30.6, 39.4, 61.5, 63.9, 70.6, 113.0, 124.2, 125.3, 126.8, 127.1, 127.7, 127.8, 129.0, 135.3, 144.0, 146.7, 157.6, 170.7 and 170.9; *m/z* [CI(NH_3)] 515 (MNH_4^+).

1,4-Bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene 13

A mixture of 1,4-bis(acetoxymethyl)-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene **10** (100 mg, 0.200 mmol) and hydrobromic acid (47%; 1.5 cm^3, 8.9 mmol) in 1,4-dioxane (10 cm^3) was heated at reflux for 2 h. After the mixture had cooled, the solvent was completely removed. The reaction mixture was redissolved in ether (100 cm^3), washed with water (4 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent was completely removed. The residue was chromatographed on silica gel using dichloromethane–light petroleum (2:1) as eluent to give 1,4-bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene **13** (81 mg, 76%). A sample for analysis was recrystallised from methanol to yield a yellow solid, mp 160 °C (Found: C, 53.4; H, 5.4; N, 2.4. $C_{24}H_{29}Br_2NO_3$ requires C, 53.45; H, 5.4; N, 2.6%); ν_{max}/cm^{-1} 1344 (NO_2), 1518 (NO_2) and 1593 (C=C); λ_{max}/nm 372 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 28851); δ_H(500 MHz; $CDCl_3$) 0.94 (3 H, m, CH_3), 0.9 (3 H, t, *J* 7, CH_3), 1.37 (4 H, m, 2 × CH_2), 1.55 (4 H, m, 2 × CH_2), 1.82 (1 H, m, CH), 3.98 (2 H, d, *J* 5, OCH_2), 4.56 (2 H, s, CH_2Br), 4.61 (2 H, s, CH_2Br), 6.87 (1 H, s, 3-H), 7.07 (1 H, d, *J* 16, vinyl-H), 7.53 (1 H, d, *J* 16, vinyl-H), 7.66 (1 H, s, 6-H) and 7.67 and 8.26 (4 H, AA′BB′, 2″-H, 3″-H, 5″-H and 6″H); δ_C(125 MHz; $CDCl_3$) 11.2, 14.1, 23.0, 24.0, 27.9, 29.1, 30.6, 31.2, 39.5, 70.7, 113.1, 124.2, 127.0, 127.4, 127.6, 127.8, 128.4, 129.0, 137.3, 143.9, 146.8 and 157.3; *m/z* [DCI(NH_3)] 537, 539, and 541 (M^+), 555, 557 and 559 (MNH_4^+).

Poly{[2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]-1,4-phenylenevinylene](1-bromoethylene)} 14

To a solution of 1,4-bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]benzene **13** (0.51 g, 0.95 mmol) in dry tetrahydrofuran (3.8 cm^3) under nitrogen was added a solution of potassium *tert*-butoxide in dry tetrahydrofuran (0.25 mol dm^{-3}; 3.6 cm^3, 0.88 mmol). The mixture was stirred for 1 h at room temperature before being poured into methanol (16 cm^3). The mixture was centrifuged for 10 min at 4500 rpm and the supernatant was removed. The residue was dissolved in dichloromethane (15 cm^3) and centrifuged at 4500 rpm for 20 min. The supernatant was then removed and filtered through a plug of cotton wool. The filtrate was added to methanol (15 cm^3) and the mixture was centrifuged at 4500 rpm for 10 min. The supernatant was removed, and the residue was washed with a small amount of methanol before being collected by dissolution in a minimum of dichloromethane. Removal of the solvent gave a reddish solid of **14** (*ca.* 221 mg, *ca.* 51%) (Found: C, 65.6; H, 6.1; N, 4.2. $C_{24}H_{28}BrNO_3$ requires C, 62.8; H, 6.1; N, 3.1%); λ_{max}(thin film)/nm 286 and 374 nm; ν_{max}(film on KBr disc)/cm^{-1} 1341 (NO_2), 1516 (NO_2) and 1592 (C=C); δ_H(500 MHz; $CDCl_3$) 0.70 (br m, CH_3), 1.13–1.78 (br m, CH and CH_2), 3.35–4.07 (br m, $ArCH_2$ and OCH_2), 5.63 (br s, CHBr), 6.54–6.84 (br m, ArH), 7.05–7.40 (br m, vinyl-H and ArH), 7.48 and 8.15 (br AA′BB′, 2″-H, 3″-H, 5″-H and 6″-H); GPC, M_n 4.3 × 10^4, M_w 3.5 × 10^5, polydispersity index 8.1.

Poly{2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]-1,4-phenylenevinylene} 15

Thin films of precursor polymer **14** were heated at 200 °C and 0.1 mmHg for 4 h to give poly{2-(2′-ethylhexyloxy)-5-[(*E*)-4″-nitrostyryl]-1,4-phenylenevinylene} **15** (Found: C, 76.5; H, 7.0; N, 3.7. $C_{24}H_{27}NO_3$ requires C, 76.4; H, 7.2; N, 3.7%); λ_{max}(thin film)/nm 294sh, 360 and 428sh; ν_{max}(film on KBr disc)/cm^{-1} 1340 (NO_2), 1516 (NO_2), and 1591 (C=C).

Conclusion

We have developed an efficient route to synthesise successfully a poly(1,4-phenylenevinylene) substituted with an electron-withdrawing group The approach allows the preparation of a soluble and processible precursor directly from a monomer containing an electron-withdrawing group which can then be easily converted to an insoluble, unprocessible conjugated polymer in the solid state The use of this polymer in opto-electronic applications is currently being investigated and the results will be reported elsewhere

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