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A New Electron-withdrawing Group Containing Poly(1,4-phenylenevinylene)

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ABSTRACT: We have synthesized and investigated the electronic properties of poly[2-(2′-ethylhexyloxy)-5-phenyl-1,4-phenylenevinylene], **12**, and its methylsulfonyl derivative poly[2-(2′-ethylhexyloxy)-5-(4″-methylsulfonylphenyl)-1,4-phenylenevinylene], **13**. Polymer **13** contains a second-order nonlinear optic chromophore which is in conjugation with the polymer backbone. Polymers **12** and **13** have been used as the electroluminescent (EL) layers in single layer light-emitting diodes (LEDs) (ITO/polymer/Al). We have found that when **12** was used, the LEDs had an external EL quantum efficiency of 0.01%. Attachment of the methylsulfonyl moiety to **12** to give **13** in an attempt to increase the electron affinity of the parent polymer was found to make no difference to the efficiency of the single layer EL devices and appeared qualitatively to reduce their lifetimes.

Introduction

The continued strong interest in developing new conjugated polymers has been driven by their potential use as the electroactive layers in light-emitting diodes (LEDs).[1] Many of the conjugated polymers investigated as the light-emitting layers in LEDs preferentially transport one of the injected charges. This generally results in an imbalance of charge injection and a poor device efficiency. One way to overcome this imbalance is based on work developed for LEDs which use small organic molecules, and it is to prepare multilayer devices in which an extra layer is introduced to block the majority charge carrier and enhance the injection of the minority charge carrier.[1−3] A second approach is to attach substituents to the polymer which enhance the affinity for the minority charge carrier. For most conjugated polymers this means increasing the electron affinity, which can be achieved by the attachment of electron-withdrawing substitutents.[1] In addition, if the polymer contains a chromophore which has an electron-donating and electron-withdrawing group then it may also be of interest for second-order nonlinear optics applications. One family of conjugated polymers which has been extensively investigated is that based on poly(1,4-phenylenevinylene) (PPV). These conjugated polymers are either produced via a processible precursor polymer or, providing they have suitable solubilizing groups, directly from the respective monomers.[1] It is interesting to note that the precursor route has been less successful for the formation of PPV derivatives with electron-withdrawing groups attached directly to the phenyl group.[4,5] In an earlier paper we reported that the precursor route could be successfully used to produce a nitro−PPV derivative in which the nitro group was connected to the polymer backbone via a conjugated styrene link.[6] In this paper we describe the synthesis of poly[2-(2′-ethylhexyloxy)-5-phenyl-1,4-phenylenevinylene], **12**, and poly[2-(2′-ethylhexyloxy)-5-(4″-methylsulfonylphenyl)-1,4-phenylenevinylene], **13**, the latter containing an electronically asymmetric chromophore with the sulfone electron-withdrawing group connected to the polymer backbone by a biphenyl link. In addition, we compare their physical and electronic properties, as well as their performance as the light-emitting layers in LEDs.

Results and Discussion

Monomer Synthesis. The first step in both monomer syntheses (Scheme 1) was the bromination of 1,4-dimethyl-2-(2′-ethylhexyloxy)benzene[6] with bromine in glacial acetic acid. This afforded the brominated derivative **1** in a 99% yield. The second step in both syntheses involved palladium catalyzed coupling of **1** with the respective arylstannanes to give biphenyls **2** and **5** in 79% and 72% yield, respectively. Here the synthetic pathways diverged with biphenyl **2** having the two methyl groups activated while biphenyl **5** required oxidation of the methyl sulfide before activation of the two benzyl positions. In the case of biphenyl **2** the compound was treated with 2.2 equiv of *N*-bromosuccinimide to give an inseparable mixture of brominated products. These were immediately acetylated using sodium acetate in glacial acetic acid before hydrolysis with sodium hydroxide in aqueous methanol. At this point the bis(alcohol) **3** could be isolated in a yield of up to 54% from biphenyl **2**. The bis(alcohol) **3** was then easily brominated forming monomer **4** using phosphorus tribromide in a 96% yield. The first step in forming the sulfone monomer **9** required the oxidation of the methyl sulfide to the sulfone. This could be achieved in a single step by reacting **5** with *m*-chloroperbenzoic acid or Oxone; however, in this direct double oxidation it was never possible to isolate **7** in a pure form. We found that a two-step oxidation, initially with Oxone, to give, after purification, the sulfoxide **6** in 90% yield, followed by a second oxidation with Oxone, gave the pure sulfone **7** in an 88% yield. The two benzyl positions of sulfone **7** were then converted to form bis(acetate) **8** by reaction with *N*-bromosuccinimide, to give the expected mixture of brominated products, followed by acetylation with sodium acetate in glacial acetic acid. Bis(acetate) **8** could

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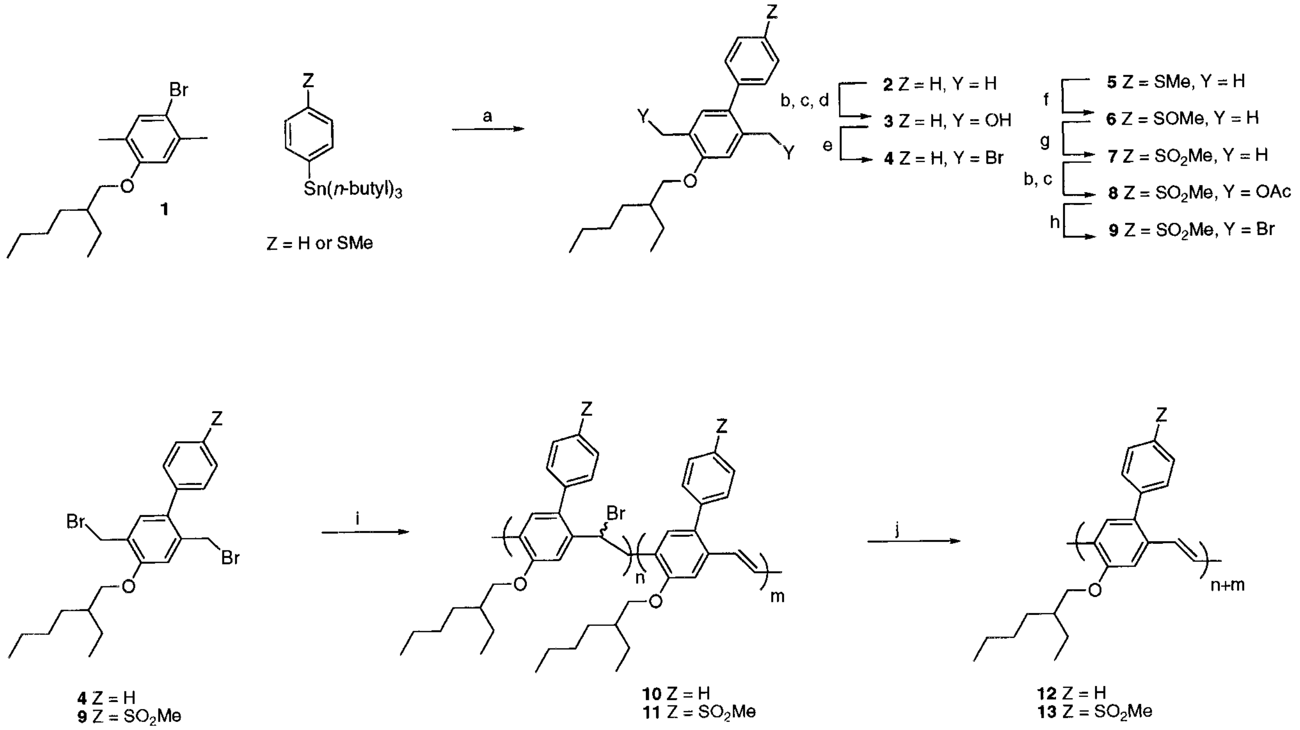
Scheme 1[a]



[a] Key: (a) Pd(OAc)$_2$, PPh$_3$, Et$_3$N, Δ; (b) NBS, CCl$_4$, AIBN, Δ; (c) NaOAc, AcOH, Δ; (d) $^-$OH(aq), MeOH, Δ; (e) PBr$_3$, CH$_2$Cl$_2$, (f) Oxone, H$_2$O, MeOH, CH$_2$Cl$_2$; (g) Oxone, H$_2$O, MeOH, CH$_2$Cl$_2$; (h) HBr(aq), 1,4-dioxane, Δ; (i) potassium *tert*-butoxide, THF, N$_2$; (j) heat, vacuum.

be purified by recrystalliztion from ethanol and under these conditions was isolated in a 30% yield. This gave an overall yield for the four steps from **5** to **8** of 24%. Alternatively it proved possible to take the impure material from the *m*-chloroperbenzoic acid oxidation of **5** to **7** through the bromination and acetylation steps to give **8**, which again could be isolated by recrystallization from ethanol, in an overall yield of 20%. Given that the yield was only slightly less than the stepwise synthesis, this procedure was used when large amounts of the sulfone monomer **9** were required. The final step in the formation of the sulfone monomer **9** was the bromination of the bis(acetate) **8**, and this was achieved in an 83% yield by treatment with hydrobromic acid in 1,4-dioxane heated at reflux.

Polymerization and Conversions. The bis(bromomethyl) monomers **4** and **9** were polymerized under the standard conditions[3,6,7,8] to give the precursor polymers **10** and **11** respectively. In each case a solution of 0.9 equiv of potassium *tert*-butoxide in tetrahydrofuran was added to a solution of **4** or **9** in tetrahydrofuran cooled in an acetone/ice bath. The reaction mixtures were then allowed to warm to room temperature and stirred for 2 h. The precursor polymers **10** and **11** were purified by reprecipitations from tetrahydrofuran using 2-propanol. Polymer **10** could also be purified by using water and 2-propanol, which assists in removing the potassium bromide formed during the reaction. We also found that **11** could be purified by precipitation from methanol without the substitution of the halide leaving group which is observed in some halo precursor polymers.[3] We also observed that in both **10** and **11** there were significant levels of conjugated segments. This arises from a competition during polymerization between the formation of the polymer and base-catalyzed elimination of the halo leaving group. In an attempt to reduce the level of conjugation in precursor polymer **11**, the polymerization was carried out at 0 °C using only 0.7 equiv of base with the subsequent workup also carried out at low temperature. This made no difference to the degree of conjugation, but it decreased the yield of polymer significantly. In the case of **10** it should also be noted that although the structure is drawn in a regioregular fashion the ^{1}H NMR spectrum shows a number of signals in the region which we would expect the methine proton of the CHBr to be found which indicates that **10** is probably a mixture of regioisomers. In contrast, **11** has only one methine signal, and we consider that this indicates that **11** is more regioregular than **10**. Polymers **10** and **11** had good solubility in tetrahydrofuran. Determination of the polymer's molecular weight by gel-permeation chromatography (gpc) against polystyrene standards was complicated. When using a Polymer Laboratory PLgel Mixed A column calibrated to $\bar{M}_p = 15 \times 10^6$ the high molecular weight components of **10** and **11** were above the calibration limit (Figure 1). We believe that the high molecular weight observed is due to the formation of polymer aggregates which are formed during the polymerization and subsequent purification.[9] As expected, the aggregation was observed to be concentration dependent. This was shown by the fact that when the concentrated solutions formed from the polymerization were diluted for gpc analysis and run immediately, then gpc traces of high molecular weight **10** and **11** were observed. However, if the solutions were diluted and equilibrated then the molecular weights decreased to $\bar{M}_w = 1.3 \times 10^5$ and $\bar{M}_n = 6.1 \times 10^4$ for **10** and $\bar{M}_w = 2.7 \times 10^5$ and $\bar{M}_n = 1.3 \times 10^5$ for **11** (Figure 1).

Thermogravimetric analysis of **10** and **11** showed that there was significant weight loss at 166 and 150 °C, respectively, which we attribute to the loss of hydrogen bromide. For polymer **10**, the conversion to **12** at 185 °C under vacuum could be easily seen by both infrared

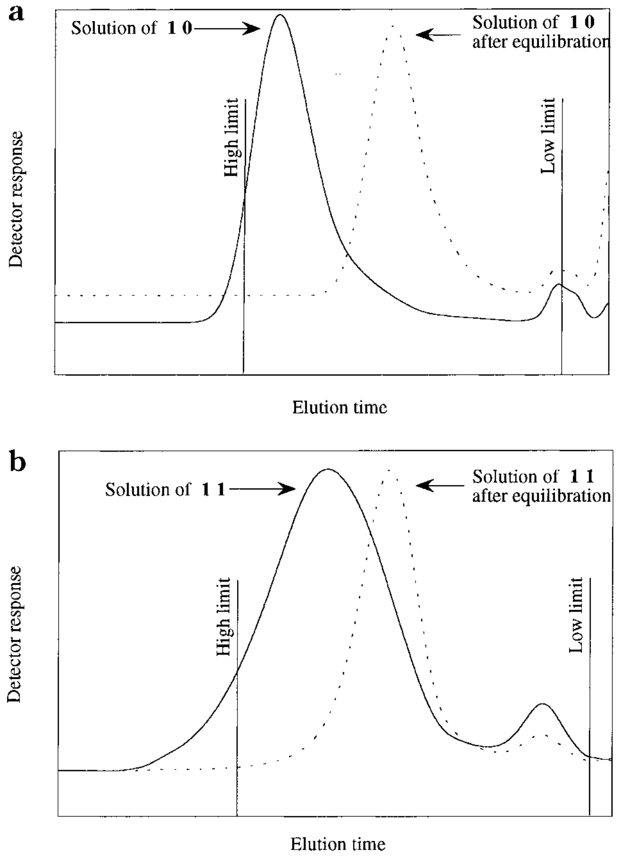


Figure 1. (a) Gel permeation chromtography traces of **10**. (b) Gel permeation chromtography traces of **11**.

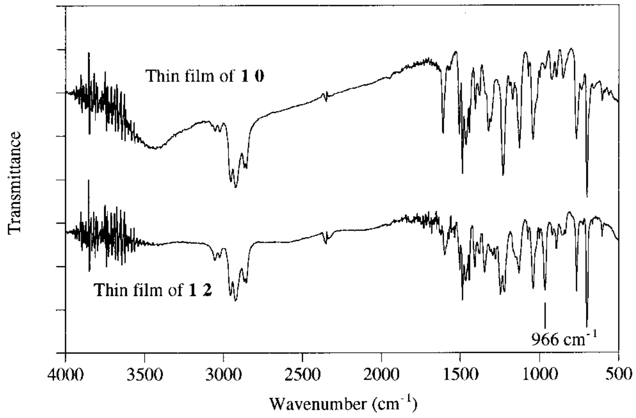


Figure 2. Infared spectra of **10** and **12**.

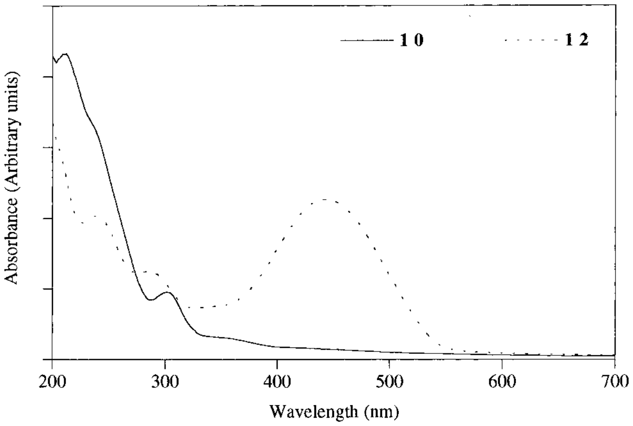


Figure 3. Solid-state UV–visible spectra of **10** and **12**.

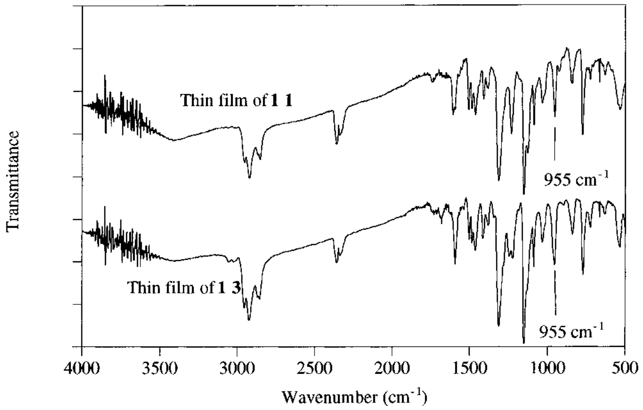


Figure 4. Infrared spectra of **11** and **13**.

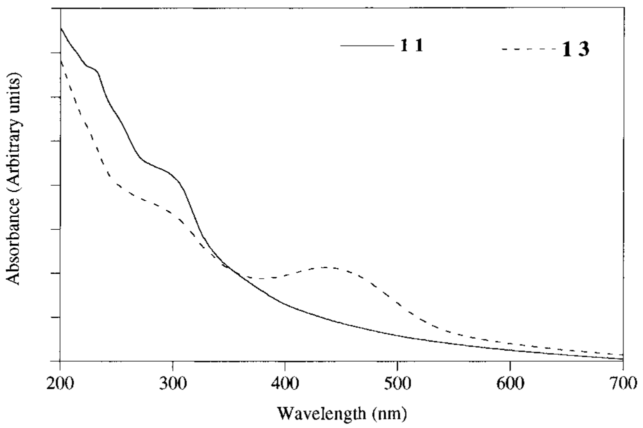


Figure 5. Solid-state UV–visible spectra of **11** and **13**.

and UV–visible spectroscopy. The infrared spectrum of **12** has a strong absorption in comparison to **10** at 966 cm^{-1}, which corresponds to the C–H stretch of a *trans*-vinylene unit (Figure 2). In addition, the UV–visible spectrum of **12** shows a new strong absorption at 444 nm (Figure 3). In contrast the conversion of **11** to **13** was more difficult to follow by infrared spectroscopy due to its more complex structure. On conversion at 160 °C, there were only small changes to the infrared spectrum in going from **11** to **13**, which might suggest that the polymer was essentially unchanged (Figure 4). However, analysis of the UV–visible spectrum in going from **11** to **13** (Figure 5) clearly shows that conversion is taking place with an increased absorption at longer wavelengths. In addition, when a film of **11** was converted to **13** at 150 °C under vacuum for 6 h, extended X-ray absorption fine structure analysis indicated that the amount of bromine had been significantly reduced, although not completely eliminated from the film. For the studies on the electronic properties of the target polymers, thin films of **10** and **11** were prepared by spin-coating from solution and converted to their respective more conjugated polymers by heating at 220 °C for 8 h under a dynamic vacuum.

Characterization of the Electronic Properties. The solid-state UV–visible absorption spectra for **12** and **13** converted at 220 °C are shown in Figure 6 for comparison. The spectra are normalized at the long wavelength absorption peak which occurs at 420 and 440 nm for **13** and **12**, respectively. The origin of the shoulder in the region of 270–300 nm in the spectra of both **12** and **13** has been attributed in part to absorbance of the isolated biphenyl and sulfonyl–biphenyl

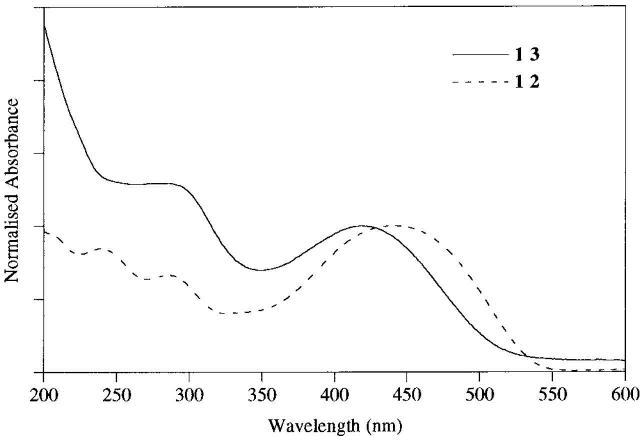


Figure 6. Solid-state UV−visible spectra for **12** and **13** converted at 220 °C.

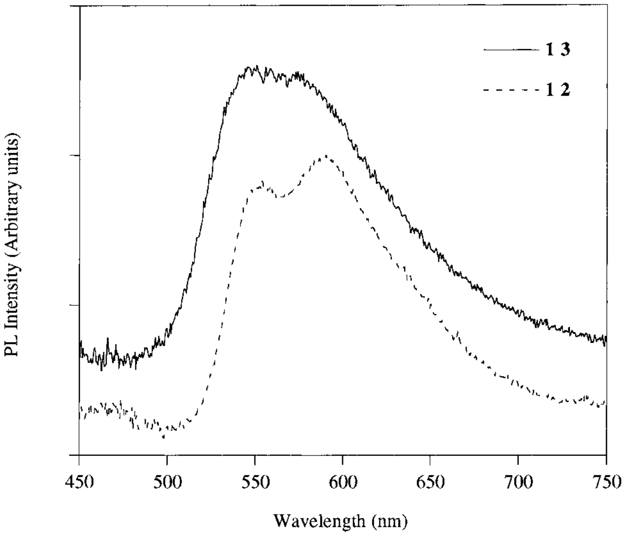


Figure 7. Solid-state photoluminescence spectra for films of **12** and **13**.

lateral chromophores. An insight into the degree of conjugation of *p*-phenylenevinylene-based polymers may be gained by comparison of the absorption at short wavelengths, near 210 nm (arising from $\pi-\pi^*$ transitions localized within individual phenyl rings), to that of the longest wavelength absorption (arising from transitions between delocalized states): the smaller the ratio the greater the conjugation. According to this relation, **12** has clearly a greater effective conjugation length than **13**. The two general reasons for reduced effective conjugation length are chemical and conformational defects. In the case of **13** both factors might be involved: incomplete conversion caused by the already partially conjugated and hence rigid structure[10] and the nonlinear optic chromophore having a more planar structure than the unsubstituted biphenyl, causing the polymer backbone to be twisted from planarity.

The solid-state photoluminescence (PL) spectra for the two polymers are shown in Figure 7. Each spectrum has been normalized to the peak maximum and then offset vertically for clarity. The PL spectrum of **12** has resolved vibronic structure with peaks at 555 and 590 nm while the spectrum for **13** has a peak at 550 nm and a shoulder at 575 nm. The red shift of the PL spectrum of **12** compared to **13** is in agreement with the shift observed in the UV−visible spectra of the two polymers and again indicates that the effective conjugation length of **12** is greater than **13**. The fact that there is vibronic structure in the PL spectra of **12** suggests that it has greater intramolecular order than **13**. The PL quantum efficiencies we found to be 24 (±2)% for **12** and 17 (±2)% for **13**. An estimate of the HOMO−LUMO band gap in these materials may be obtained from the point at which the normalized absorption and emission spectra intersect. The HOMO−LUMO band gaps for **12** and **13** are 2.38 and 2.45 eV, respectively. Given that the HOMO−LUMO energy gap and PL quantum efficiencies of the two polymers are similar, it might be expected that any difference in the EL quantum efficiency would be due to the methyl sulfone group.

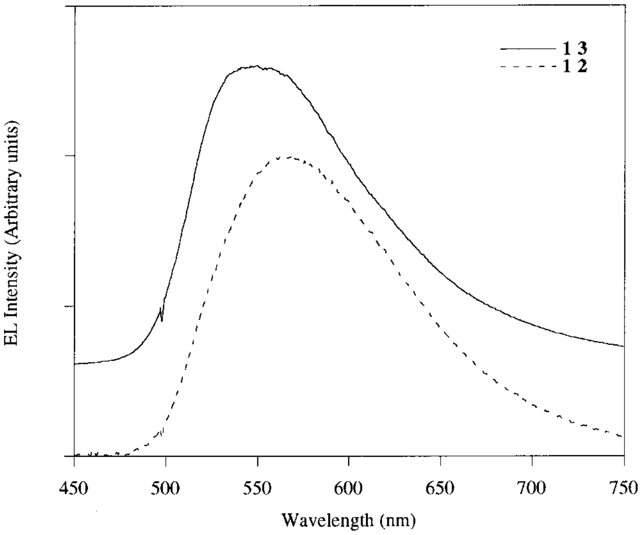


Figure 8. Electroluminescence spectra from ITO/**12** or **13**/Al device structures.

Single layer EL devices were fabricated with the polymer films sandwiched between an indium tin oxide (ITO) anode and an aluminum cathode. Precursor polymer solutions were spin-coated onto ITO and then thermally converted to give the conjugated polymers. Aluminum electrodes were then evaporated on top of the polymer film to complete the devices. Electroluminescence (EL) was observed from both polymer devices and the spectra are shown in Figure 8. The EL spectra from the ITO/**12**/Al and ITO/**13**/Al devices are broad with peaks at 560 and 550 nm respectively, and as a consequence emission from both devices appeared green to the eye. The EL spectra mirror the red shift observed in the PL spectra but the vibronic structure which was clearly resolved for **12** in the PL spectrum is lost in device emission. The current density vs applied field characteristics for the EL devices are shown in Figure 9. Despite strong similarities in the chemical structures of the polymers they behave very differently under an applied bias. The ITO/**13**/Al device shows a reproducible "current anomaly" at low bias. This corresponds to an apparent overshoot in the current drawn through the device at low bias and though its origin has not been identified may be a result of poor film uniformity or adhesion to the substrate. The onset of EL occurs just beyond this "anomaly". For comparison of the two polymers we define the threshold field as the field required to obtain a current density of 10 mA/cm^2. For **13** (film thickness approximately 70 nm) the threshold field was 1.7 MV/cm while **12** (film thickness approximately 120 nm) had a threshold field of 1.98 MV/cm. In the ITO/**13**/Al device the peak luminance obtained was 60 cd/m^2 at a current density of 200 mA/

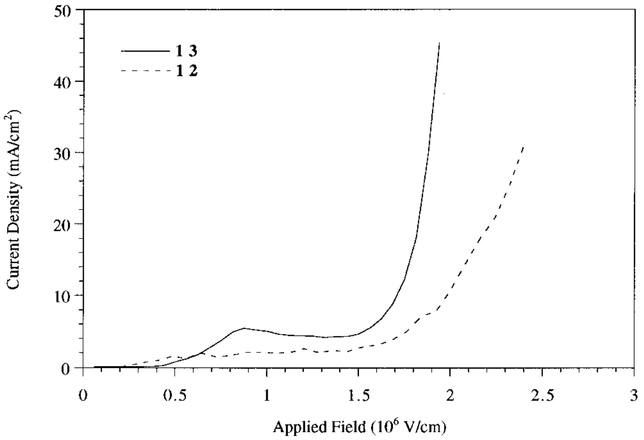


Figure 9. Current density vs applied field characteristics of ITO/**12**/Al and ITO/**13**/Al.

cm^2, corresponding to a peak external quantum efficiency of 0.01%. The EL was unstable and inhomogeneous with device lifetimes of the order of seconds. In the ITO/**12**/Al device a peak luminance of 20 cd/m^2 was recorded at a current density of 58.5 mA/cm^2, corresponding to an external quantum efficiency of 0.01%. The uniformity of the EL emission was much improved and the devices were qualitatively more stable under these conditions. These results appear to indicate that the sulfone moiety has little effect on the electron affinity of the polymer. This could be the result of the steric interactions around the biphenyl link reducing the degree of conjugation that the electron-withdrawing group has with the polymer backbone.

Conclusions

We have developed an efficient precursor polymer route to a PPV derivative which contains an electron-withdrawing sulfone group connected to the polymer backbone via a biphenyl link. There are distinct differences in the optical properties of the parent and sulfone containing polymers, although the PL efficiencies are similar. Both polymers have been successfully used as the light-emitting layers in LEDs. However, the sulfone group was found not to improve the EL efficiencies in single layer devices.

Experimental Section

Measurements. NMR spectra were recorded either on Bruker 500 or 250 MHz spectrometers. ^{13}C NMR spectra were fully decoupled. IR spectra were recorded on a Perkin-Elmer 781 or Paragon 1000 Infrared spectrometer. All spectra were recorded as a solution in distilled chloroform unless otherwise stated. UV−visible spectra were recorded on Perkin-Elmer UV−visible (Lambda 2 or 14P) or Unicam UV4 UV−visible spectrometers and unless otherwise stated all spectra were recorded as a solution in distilled chloroform. Mass spectra were recorded on a VG 20−250 instrument, the mode of ionization 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 or Mr. R. Prior in the Dyson Perrins Laboratory. Gel permeation chromatography was carried out using PLgel 20μm Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($\bar{M}_p = 1300$ to 15.4×10^6) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed with helium and pumped at a rate of 1 mL/min at 22 ± 1 °C.

Single layer EL devices were fabricated with the polymer film sandwiched between an indium tin oxide (ITO) anode and an aluminum cathode. Precursor polymer solutions (≈10−15 mg/mL in dry tetrahyrofuran) were spin coated onto precleaned ITO/glass substrates at a spin speed of 2000 rpm for 40 s. Thermal conversion of the precursor films was achieved by heating to 220 °C in vacuo (10^{-6} mbar) for 8 h. Aluminum electrodes were then evaporated on top of the polymer film at 10^{-6} mbar. Electroluminescence and current−voltage measurements were carried out in an evacuated sample chamber ($<10^{-2}$ mbar). Electroluminescence measurements were carried out under forward bias with the ITO and aluminum electrodes biased positive and negative, respectively. Light output was viewed in a forward direction through the semitransparent ITO electrode. The luminance characteristic was measured by a silicon photodiode. Spectral characteristics were recorded using an optical fiber coupled to a CCD spectrograph. Absolute luminance measurements were recorded using a Topcon BM 8 luminance meter. External quantum efficiencies were calculated using a standard equation involving the ratio of the absolute luminance in a forward direction to the current density drawn by the device, taking into account the spectral characteristics of the emitted light and the photopic efficacy of the detector. The PL excitation source was a He:Cd laser with an excitation wavelength of 442 nm. Absorption and PL spectra were measured on polymer films spin-coated onto quartz substrates. PL quantum efficiency measurements were performed within a fully calibrated integrating sphere flushed with nitrogen to avoid photooxidation. Film thickness measurements were measured using a Dektak^3 ST surface profiler.

Synthesis. 1-Bromo-2,5-dimethyl-4-(2′-ethylhexyloxy)-benzene, 1. A solution of bromine (24.0 g, 0.15 mol) in glacial acetic acid (280 mL) was added to a solution of 1,4-dimethyl-2-(2′-ethylhexyloxy)benzene (32.5 g, 0.13 mol) in methanol (650 mL) and cooled to 0 °C, and the reaction mixture was stirred for 2 h. The reaction mixture was basified by addition to sodium carbonate solution (10%, 1000 mL) and extracted with dichloromethane (2 × 500 mL). The combined organic layers were washed with water (200 mL), dried over anhydrous sodium sulfate, and the solvent was partially removed. The remaining solution was passed through a silica plug, and then the solvent was completely removed to yield the pale yellow oil **1** (42.5 g, 99%). Anal. Calcd for $C_{16}H_{25}BrO$: C, 61.35; H, 8.0. Found: C, 61.6; H, 8.4. Characterization: λ_{max} (CH_2Cl_2)/nm 284 (ϵ/dm^3 mol^{-1} cm^{-1} 3516); δ_H (250 MHz, $CDCl_3$) 0.94 (6 H, m, 2 × CH_3), 1.31−1.55 (8 H, m, 4 × CH_2), 1.76 (1 H, m, CH), 2.16 (3 H, s, CH_3), 2.36 (3 H, s, CH_3), 3.82 (2 H, d, *J* 5, OCH_2), 6.69 (1 H, s, ArH), 7.26 (1 H, s, ArH); δ_C (125 MHz, $CDCl_3$) 11.2, 14.1, 15.5, 22.9, 23.0, 24.1, 29.1, 30.7, 39.5, 70.4, 113.3, 114.2, 126.3, 133.5, 135.5, 156.6; *m*/*z* (CI$^+$/NH_3) 312 and 314 (M$^+$).

1,4-Dimethyl-2-(2′-ethylhexyloxy)-5-phenylbenzene, 2. Bromobenzene **1** (3.64 g, 11.6 mmol), palladium acetate (134 mg, 0.60 mmol), and triphenylphosphine (488 mg, 1.86 mmol) were mixed in dry triethylamine (20 mL) and stirred at room temperature under nitrogen. Tri-*n*-butylphenyl stannane (5.12 g, 13.9 mmol) in dry triethylamine (10 mL) was added dropwise at room temperature. The reaction mixture was then stirred at reflux for 15 h. After cooling, diethyl ether (200 mL) was added, the solution was filtered through Celite and the solvent was removed. The residue was chromatographed on silica gel using dichloromethane-petroleum ether (1:9) as eluent to give a colorless oil containing impure product. The residue was purified by distillation to yield the colorless oil **2** (2.84 g, 79%), bp 215 °C at 0.2 mmHg. Anal. Calcd for $C_{22}H_{30}O$: C, 85.1; H, 9.7. Found: C, 85.2; H, 9.9. Characterization: λ_{max} ($CHCl_3$)/nm 257 (ϵ/dm^3 mol^{-1} cm^{-1}, 9475); δ_H (500 MHz; $CDCl_3$) 0.92−0.99 (6 H, m, 2 × CH_3), 1.27−1.42 (4 H, m, 2 × CH_2), 1.45−1.58 (4 H, m, 2 × CH_2), 1.75−1.80 (1 H, m, CH), 2.23 (3 H, s, CH_3), 2.27 (3 H, s, CH_3), 3.91 (2 H, d, *J* 5, OCH_2), 6.73 (1 H, s, 2-H), 7.03 (1 H, s, 6-H), 7.32 (3 H, m, ArH), 7.39 (2 H, m, ArH); δ_C (125 MHz; $CDCl_3$) 11.2, 14.1, 15.7, 20.4, 23.1, 24.1, 29.1, 30.7, 39.6, 70.2, 112.6, 124.0, 126.3, 127.9, 129.4, 132.0, 133.4, 133.5, 142.0, 156.5; *m*/*z* [CI(NH_3)] 311 (100, MH$^+$).

1,4-Bis(hydroxymethyl)-2-(2′-ethylhexyloxy)-5-phenylbenzene, 3. A solution of biphenyl **2** (2.30 g, 7.36 mmol), *N*-bromosuccinimide (2.97 g, 16.5 mmol) and 2,2′-azobis-(2-methylpropionitrile) (100 mg) in carbon tetrachloride (230 mL) was heated at reflux for 4 h. After cooling, the solution was filtered and the solvent was removed to give a yellow oily solid (4.68 g) containing a mixture of brominated products. A mixture of the crude residue (4.68 g) and anhydrous sodium acetate (3.59 g, 43.7 mmol) in glacial acetic acid (75 mL) was heated at reflux for 16 h. After cooling, the solvent was removed to give a brown oily solid. Dichloromethane (150 mL) was added, the organic layer was washed with water (3 × 150 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed to give a brown oil (3.08 g) containing a mixture of acetylated products. A mixture of the crude residue (3.08 g), methanol (115 mL), and aqueous sodium hydroxide solution (10%, 20 mL) was heated at reflux for 2 h. After cooling, the solvent was removed to give a brown oily solid. Dichloromethane (100 mL) was added, the organic layer was washed with water (2 × 100 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed to give a brown oil (2.46 g). The residue was chromatographed on silica gel using dichloromethane−ethyl acetate (95:5) as eluent to yield the pale yellow solid **3** (1.36 g, 54%), mp 98 °C. Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.2; H, 8.8. Found: C, 77.3; H, 8.5. Characterization: υ_{max} (CH_2Cl_2)/cm^{-1} 3600 (OH); λ_{max} ($CHCl_3$)/nm 251 (ϵ/dm^3 mol^{-1} cm^{-1}, 11460); δ_H (500 MHz; $CDCl_3$) 0.92−0.99 (6 H, m, 2 × CH_3), 1.36 (4 H, m, 2 × CH_2), 1.46−1.57 (4 H, m, 2 × CH_2), 1.69 (1 H, br s, OH), 1.80 (1 H, m, CH), 2.42 (1 H, br s, OH), 4.02 (2 H, m, OCH_2), 4.62 (2 H, CH_2OH), 4.73 (2 H, CH_2OH), 7.13 (1 H, s, 2-H), 7.21 (1 H, s, 6-H), 7.32 (3 H, m, ArH), 7.41 (2 H, m, Ar H); δ_C (125 MHz; $CDCl_3$) 11.2, 14.0, 23.0, 24.2, 29.1, 30.8, 39.5, 62.0, 63.1, 70.4, 110.5, 127.0, 128.2, 128.4, 129.3, 130.3, 133.2, 138.6, 140.3, 156.7; *m/z* [EI] 342 (50, M$^+$).

1,4-Bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-phenylbenzene, 4. Phosphorus tribromide (8.55 g, 31.5 mmol) was added to a solution of bis(hydroxymethyl)biphenyl (**3**) (3.66 g, 10.7 mmol) in dry dichloromethane (150 mL) cooled in an ice bath under argon. The reaction mixture was stirred with ice bath cooling for 2 h and then at room temperature for 66 h. Water (150 mL) was added and the organic layer separated. The organic layer was washed with water (150 mL) and dried over anhydrous sodium sulfate and the solvent completely removed. The residue was dissolved in dichloromethane (50 mL) and filtered through a plug of silica and the solvent removed to yield the white solid **4** (4.82 g, 96%), mp 68 °C. Anal. Calcd for $C_{22}H_{28}Br_2O$: C, 56.4; H, 6.0. Found: C, 56.4; H, 6.0. Characterization: λ_{max} ($CHCl_3$)/nm 311 (ϵ/dm^3 mol^{-1} cm^{-1}, 3687); δ_H (500 MHz; $CDCl_3$) 0.94 (3 H, m, CH_3), 0.99 (3 H, t, *J* 7, CH_3), 1.38 (4 H, m, 2 × CH_2), 1.49−1.64 (4 H, m, 2 × CH_2), 1.83 (1 H, m, CH), 4.00 (2 H, d, *J* 5, OCH_2), 4.44 (2 H, s, CH_2Br), 4.55 (2 H, s, CH_2Br), 7.02 (1 H, s, 2-H), 7.24 (1 H, s, 6-H), 7.36−7.46 (5 H, m, 2″−H, 3″−H, 4″−H, 5″−H and 6″−H); δ_c (125 MHz; $CDCl_3$) 11.3, 14.1, 23.0, 24.1, 28.2, 29.1, 30.7, 32.2, 39.5, 70.5, 113.3, 126.7, 127.3, 128.3, 129.2, 132.6, 134.3, 136.8, 139.5, and 156.6; *m/z* [EI] 466, 468, 470 (M$^+$).

Poly[{(2-[2′-ethylhexyloxy]-5-phenyl-1,4-phenylene)[1-bromoethylene]}-*co*-{2-[2′-ethylhexyloxy]-5-phenyl-1,4-phenylenvinylene}], 10. A solution of potassium *tert*-butoxide dissolved in dry tetrahydrofuran (0.3 M, 3.3 mL, 0.97 mmol) was added to a stirred solution of bis(bromomethyl)-biphenyl **4** (0.504 g, 1.08 mmol) in dry tetrahydrofuran (3.6 mL) cooled in an acetone/ice bath under nitrogen. A bright yellow viscous solution was formed. The reaction mixture was allowed to warm to room temperature after 10 min and stirred for 2 h. Polymer **10** was precipitated by adding the reaction mixture dropwise to ice-cooled 2-propanol (50 mL). The mixture was filtered and the residue, polymer **10**, was briefly dried at the pump. The residue was dissolved in dry tetrahydrofuran and the polymer was precipitated again by addition to an excess of 2-propanol. The mixture was filtered and the residue collected. The procedure was then repeated a further two times to yield a yellow/orange solid of **10** which contained some solvent (≈300 mg, ≈60%). Characterization: λ_{max} ($CHCl_3$)/nm 210 and 301; δ_H (500 MHz; $CDCl_3$) 0.71−0.96 (br m, CH_3), 1.13−1.76 (br m, CH and CH_2), 3.00−4.04 (br m, ArCH_2 and OCH_2), 4.94−5.12, 5.15−5.31, and 5.59−5.76 (br, CHBr), 6.28 (br d, ArH or vinyl H), 6.38−6.91 (br m, ArH and vinyl H), and 6.95−7.50 (br m, ArH and vinyl H); Gel permeation chromatography of equilibrated sample: $\bar{M}_w = 1.3 \times 10^5$ and $\bar{M}_n = 6.1 \times 10^4$, pd = 2.1.

Poly{2-(2′-ethylhexyloxy)-5-phenyl-1,4-phenylenevinylene}, 12. Thin films of **10** were heated at 185 °C under a dynamic vacuum for 14 h to yield **12**. Characterization: υ_{max}(film on KBr disk)/cm^{-1} 966 (C=CH); λ_{max}(thin film)/nm 239, 285, and 444.

1,4-Dimethyl-2-(2′-ethylhexyloxy)-5-(4″-thioanisole)-benzene, 5. Bromobenzene **1** (30.0 g, 94.6 mmol), palladium acetate (490 mg, 2 mol %), and triphenylphosphine (1.99 g, 8 mol %) were mixed in dry triethylamine (20 mL) and degassed under nitrogen. Tri-*n*-butyl(4-thioanisole) stannane[11] (46.9 g, 0.114 mol) in dry triethylamine (10 mL) was added, and the reaction mixture was heated at reflux for 16 h. After cooling, the solvent was removed and diethyl ether (50 mL) was added. The solution was filtered through Celite and the solvent removed to give a dark yellow oil. The residue was chromatographed on silica gel using dichloromethane−petroleum ether (1:9) as eluent to give a colorless oil (39.3 g). Further purification by distillation yielded the colorless oil **5** (31.2 g, 92%), bp 250 °C at 0.4 mmHg. Anal. Calcd for $C_{23}H_{32}OS$: C, 77.5; H, 9.05. Found: C, 77.6; H, 9.25. Characterization: λ_{max} ($CHCl_3$)/nm 277 (ϵ/dm^3 mol^{-1} cm^{-1}, 22 500); δ_H (500 MHz; $CDCl_3$) 0.91−0.98 (6 H, m, 2 × CH_3), 1.35 (4 H, m, 2 × CH_2), 1.47−1.59 (4 H, m, 2 × CH_2), 1.77 (1 H, m, CH), 2.22 (3 H, s, CH_3), 2.26 (3 H, s, CH_3), 2.53 (3 H, s, SCH_3), 3.89 (2 H, d, *J* 5, OCH_2), 6.72 (1 H, s, 3-H), 7.00 (1 H, s, 6-H), 7.23 and 7.30 (4 H, AA′BB′, 2″−H, 3″−H, 5″−H and 6″−H); δ_C (125 MHz; $CDCl_3$) 11.3, 14.1, 15.7, 16.0, 20.5, 23.1, 24.1, 29.1, 30.7, 39.6, 70.2, 112.6, 124.1, 126.4, 129.9, 131.9, 132.8, 133.5, 136.1, 138.9, 156.6; *m/z* [CI(NH_3)] 357 (100, MH$^+$).

1,4-Dimethyl-2-(2′-ethylhexyloxy)-5-(4″-methylsulfinylphenyl)benzene, 6. A solution of Oxone (47%, 4.5 g, 14.0 mmol) in water (38 mL) was added to a solution of thioanisolebiphenyl **5** (2.50 g, 6.94 mmol) in a mixture of dichloromethane (25 mL) and methanol (38 mL) cooled to 0 °C. The solution was allowed to warm to room temperature over 2 h and then extracted with chloroform (3 × 75 mL). The combined organic layers were washed with water (3 × 100 mL) and brine (100 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed to give a colorless oil (2.94 g). The residue was chromatographed on silica gel using dichloromethane−ethyl acetate (1:0−1:1) as eluent to yield the colorless oil **6** (2.35 g, 90%), bp 250 °C at 0.45 mmHg. Characterization: υ_{max} (thin film)/cm^{-1} 1050 and 1087 (S=O); λ_{max} ($CHCl_3$)/nm 280 (ϵ/dm^3 mol^{-1} cm^{-1}, 5684); δ_H (500 MHz; $CDCl_3$) 0.91−0.98 (6 H, m, 2 × CH_3), 1.35 (4 H, m, 2 × CH_2), 1.42−1.59 (4 H, m, 2 × CH_2), 1.77 (1 H, m, CH), 2.23 (3 H, s, CH_3), 2.26 (3 H, s, CH_3), 2.79 (3 H, s, $SOCH_3$), 3.91 (2 H, d, *J* 5, OCH_2), 6.73 (1 H, s, 3-H), 7.01 (1 H, s, 6-H) and 7.47 and 7.68 (4 H, AA′BB′, 2″-H, 3″-H, 5″-H, and 6″-H); δ_C (125 MHz; $CDCl_3$) 11.2, 14.1, 15.7, 20.4, 23.1, 24.1, 29.1, 30.7, 39.6, 43.9 70.3, 112.7, 123.3, 124.4, 130.4, 131.8, 132.0, 133.5, 143.4, 145.2, 157.1; *m/z* [CI(NH_3)] 244 (36%), 245 (100), 260 (25), 372 (27, M$^+$), 373 (35, MH$^+$); exact mass 373.2205, $C_{23}H_{33}O_2S$ (MH$^+$) requires 373.2201.

1,4-Dimethyl-2-(2′-ethylhexyloxy)-5-(4″-methylsulfonylphenyl)benzene, 7. A solution of Oxone (47%, 2.56 g, 7.92 mmol) in water (11 mL) was added to a solution of methylsulfinylbiphenyl, **6** (0.50 g, 1.32 mmol), in a mixture of dichloromethane (7 mL) and methanol (11 mL), cooled to 0 °C. The solution was allowed to warm to room temperature over 15 h and then extracted with chloroform (3 × 100 mL). The combined organic layers were washed with water (3 × 100 mL) and brine (100 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed to give a white oily solid (542 mg). The residue was chromatographed on silica gel using dichloromethane−ethyl acetate (4:1−0:1) as eluent to yield the white solid **7** (457 mg, 88%), mp 65 °C. Anal. Calcd for $C_{23}H_{32}O_3S$: C, 71.1; H, 8.25. Found: C, 71.2; H, 8.5. Characterization: υ_{max} (CH_2Cl_2)/cm^{-1} 1154 (SO_2) and 1315 (SO_2); λ_{max} ($CHCl_3$)/nm 290 (ϵ/dm^3 mol^{-1} cm^{-1}, 17 800); δ_H (500 MHz; $CDCl_3$) 0.92−0.99 (6 H, m, 2 × CH_3), 1.36 (4 H, m, 2 × CH_2), 1.43−1.60 (4 H, m, 2 × CH_2), 1.78 (1 H, m, CH), 2.24 (3 H, s, CH$_3$), 2.27 (3 H, s, CH$_3$), 3.11 (3 H, s, SO$_2$CH$_3$), 3.90 (2 H, d, *J* 5, OCH$_2$), 6.75 (1 H, s, 3-H), 7.00 (1 H, s, 6-H), and 7.51 and 7.96 (4 H, AA′BB′, 2″-H, 3″-H, 5″-H, and 6″-H); δ_{C} (125 MHz; CDCl$_3$) 11.2, 14.0, 15.7, 20.4, 23.0, 24.1, 29.1, 30.7, 39.6, 44.6, 70.3, 112.8, 124.6, 127.1, 130.3, 131.4, 131.7, 133.5, 138.3, 147.9, 157.3; *m/z* [CI(NH$_3$)] 276 (25%), 388 (62, M$^+$), 406 (100, MNH$_4^+$).

1,4-Bis(acetoxymethyl)-2-(2′-ethylhexyloxy)-5-(4″-methylsulfonylphenyl)benzene, 8. Method 1. A solution of methylsulfonylbiphenyl **7** (840 mg, 2.16 mmol), *N*-bromosuccinimide (818 mg, 4.45 mmol), and 2,2′-azobis-(2-methylpropionitrile) (20 mg) in ethanol-free chloroform was heated at reflux for 2 h. After cooling, the solvent was removed to give a yellow solid (2.51 g) which was chromatographed on silica gel using dichloromethane as eluent to give a white solid (1.64 g) containing a mixture of brominated products. A mixture of the white solid (1.64 g) and anhydrous sodium acetate (766 mg, 9.34 mmol) in glacial acetic acid (18 mL) was heated at reflux for 2 h. After cooling, the solvent was removed to give a yellow oily solid. Ether (100 mL) was added, and the organic layer was washed with water (4 × 100 mL), dried over anhydrous sodium sulfate, and filtered and the solvent removed to give a yellow oil (960 mg). Recrystallization from ethanol yielded the white solid **8** (308 mg, 30%), mp 86 °C. Anal. Calcd for C$_{27}$H$_{36}$O$_7$S: C, 64.3; H, 7.2. Found: C, 64.5; H, 7.0. Characterization: $\upsilon_{\max}$ (CH$_2$Cl$_2$)/cm^{-1} 1154 (SO$_2$), 1317 (SO$_2$), and 1738 (C=O); $\lambda_{\max}$ (CHCl$_3$)/nm 279 (ϵ/dm^3 mol^{-1} cm^{-1}, 13351); δ_{H} (500 MHz; CDCl$_3$) 0.92–0.99 (6 H, m, 2 × CH$_3$), 1.35 (4 H, m, 2 × CH$_2$), 1.45–1.55 (4 H, m, 2 × CH$_2$), 1.77 (1 H, m, CH), 2.08 (3 H, s, CH$_3$CO$_2$), 2.10 (3 H, s, CH$_3$CO$_2$), 3.12 (3 H, s, CH$_3$SO$_2$), 3.96 (2 H, m, OCH$_2$), 4.99 (2 H, s, CH$_2$OCO), 5.19 (2 H, s, CH$_2$OCO), 7.04 (1 H, s, 3-H), 7.25 (1 H, s, 6-H) and 7.55 and 8.00 (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, 24.0, 29.1, 30.6, 39.5, 44.6, 61.4, 64.1, 70.6, 112.6, 125.0, 127.4, 130.3, 131.1, 132.3, 134.4, 139.3, 145.9, 157.3, 170.5, 170.8; *m/z* [CI(NH$_3$)] 504 (M$^+$) and 522 (MNH$_4^+$).

Method 2. *m*-Chloroperoxybenzoic acid (50%, 2.10 g, 6.09 mmol) was added to a solution of thioanisolebiphenyl **5** (1.00 g, 2.78 mmol) in dichloromethane (36 mL) which had been cooled to −10 °C. The reaction mixture was allowed to warm to room temperature with stirring over 15 h and then was washed with sodium bicarbonate solution (5%, 8 × 100 mL) and water (100 mL) and dried over anhydrous sodium sulfate, filtered, and the solvent was removed to give a yellow oil. The oil was dissolved in dichloromethane (100 mL), filtered through a plug of silica, and then the solvent was removed to give a yellow oil (750 mg) containing the sulfone. A mixture of the crude sulfone (750 mg), *N*-bromosuccinimide (906 mg, 5.85 mmol), and 2′2′-azobis-(2-methylpropionitrile) (100 mg) in carbon tetrachloride (16 mL) was heated at reflux for 2 h. After cooling, the solution was filtered and the solvent was removed to give a yellow oily solid (1.97 g) containing a mixture of brominated products. A mixture of the crude residue (1.97 g) and anhydrous sodium acetate (671 mg, 8.18 mmol) in glacial acetic acid (16 mL) was heated at reflux for 1 h. After cooling, the solvent was removed to give a brown oily solid. Ether (50 mL) was added, and the organic layer was washed with water (5 × 100 mL), dried over anhydrous sodium sulfate, and filtered and the solvent removed to give a yellow oil (990 mg). The residue was recrystallized from ethanol to give **8** (267 mg, 20%), a sample of which co-chromatographed with and had identical ^{1}H NMR spectrum to an authentic sample.

1,4-Bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-(4″-methylsulfonylphenyl)benzene, 9. A mixture of bis(acetoxymethyl)methylsulfonylbiphenyl (**8**) (1.20 g, 2.49 mmol), hydrobromic acid (47%, 18 mL), and 1,4-dioxane (120 mL) was heated at reflux for 2 h. After cooling, the solvent was removed and ether (100 mL) was added. The organic layer was washed with water (3 × 100 mL), dried over anhydrous sodium sulfate, and filtered and the solvent removed to give a pale yellow oil. The residue was chromatographed on silica gel using dichloromethane as eluent to yield the white solid **9** (1.14 mg, 83%), mp 108 °C. C$_{23}$H$_{30}$Br$_2$O$_3$S: C, 50.6; H, 5.5. Found: C, 50.65; H, 5.5. Characterization: $\upsilon_{\max}$ (CH$_2$Cl$_2$)/cm^{-1} 1154 (SO$_2$) and 1317 (SO$_2$); $\lambda_{\max}$ (CHCl$_3$)/nm 278 (ϵ/dm^3 mol^{-1} cm^{-1}, 25 513) and 278 sh (20 270); δ_{H} (500 MHz; CDCl$_3$) 0.94 (3 H, m, CH$_3$), 0.99 (3 H, t, *J* 7, CH$_3$), 1.37 (4 H, m, 2 × CH$_2$), 1.47–1.63 (4 H, m, 2 × CH$_2$), 1.83 (1 H, m, CH), 3.13 (3 H, s, CH$_3$SO$_2$), 4.01 (2 H, d, *J* 5, OCH$_2$), 4.37 (2 H, s, CH$_2$Br), 4.54 (2 H, s, CH$_2$Br), 7.03 (1 H, s, 3-H), 7.22 (1 H, s, 6-H), 7.65 and 8.03 (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, 27.7, 29.1, 30.6, 31.4, 39.5, 44.5, 70.6, 113.6, 127.2, 127.5, 130.2, 132.0, 132.3, 136.8, 139.5, 145.3, 157.2; *m/z* [CI-(NH$_3$)] 58 (45%), 165 (48), 195 (77), 196 (62), 276 (48), 387 (72), 406 (100), 484 (49), 562 (33, MNH$_4^+$), 564 (70, MNH$_4^+$), 566 (32, MNH$_4^+$).

Poly[{(2-[2′-ethylhexyloxy]-5-[4″-methylsulfonylphenyl]-1,4-phenylene)[1-bromoethylene]}-*co*-{2-[2′-ethylhexyloxy]-5-[4″-methylsulfonylphenyl]-1,4-phenylenevinylene}], 11. A solution of potassium *tert*-butoxide dissolved in dry tetrahydrofuran (0.3 M, 2.6 mL, 0.8 mmol) was added to a solution of bis(bromomethyl)methylsulfonylbiphenyl **9** (0.5 g, 0.9 mmol) in dry tetrahydrofuran (3 mL) cooled in an acetone/ice bath under nitrogen. A bright yellow viscous solution was formed, and dry tetrahydrofuran (4 mL) was added. The reaction mixture was allowed to warm to room temperature after 10 min and stirred for 2 h. A small amount of a precipitate was formed. The reaction mixture was filtered through a plug of cotton wool, and the polymer **11** was precipitated by adding the reaction mixture dropwise to ice-cold 2-propanol (50 mL). The mixture was centrifuged for 10 min at 4000 rpm, and the supernatant was removed. The crude polymer **11** was briefly dried under vacuum, dissolved in dry tetrahydrofuran, and then precipitated by addition to an excess of 2-propanol. The solid was collected after centrifugation, and the process was repeated a further two times. The residue was finally collected by dissolution in a minimum of tetrahydrofuran, and the solvent was removed to leave **11** as an orange/yellow solid (≈200 mg, ≈40%). Characterization: $\upsilon_{\max}$ (thin film)/cm^{-1} 955 (HC=C), 1154 (SO$_2$), 1315 (SO$_2$); $\lambda_{\max}$ (CH$_2$Cl$_2$)/nm 300sh; δ_{H} (500 MHz: CDCl$_3$) 0.74–1.00 (br m, CH$_3$), 1.14–1.90 (br m, CH and CH$_2$), 2.94–3.25 and 3.30–4.10 (br m, CH$_3$SO$_2$, OCH$_2$, and ArCH$_2$), 5.05–5.23 (br s, CHBr), 6.27–7.63 (br m, ArH or vinyl H), 7.67–8.05 (br m, ArH)); gel permeation chromatography of equilibrated sample, $\bar{M}_{\mathrm{w}} = 2.7 \times 10^5$ and $\bar{M}_{\mathrm{n}} = 1.3 \times 10^5$, pd = 2.1.

Poly{2-[2′-ethylhexyloxy]-5-[4″-methylsulfonylphenyl]-1,4-phenylenvinylene}], 13. Thin films of **11** were heated at 160 °C under a dynamic vacuum for 14 h to yield **13**. Characterization: $\upsilon_{\max}$ (film on KBr disk)/cm^{-1} 955 (C=CH), 1154 (SO$_2$), 1315 (SO$_2$); $\lambda_{\max}$ (thin film)/nm 285 sh, 437.

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