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Chemical Tuning of the Electronic Properties of Poly(*p*-phenylenevinylene)-Based Copolymers

Paul L. Burn,[†] Arno Kraft,[†] Derek R. Baigent,[‡] Donal D. C. Bradley,[‡] Adam R. Brown,[‡] Richard H. Friend,[‡] Richard W. Gymer,[‡] Andrew B. Holmes,[*,†] and Roger W. Jackson[†]

Contribution from the University Chemical Laboratory,
Lensfield Road, Cambridge, CB2 1EW, United Kingdom, and Cavendish Laboratory,
Madingley Road, Cambridge, CB3 0HE, United Kingdom

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Abstract: Molecular engineering has allowed the control of the HOMO–LUMO gap energy in a family of conjugated polymers based on poly(*p*-phenylenevinylene) (PPV). Random copolymerization of **1** and **6** afforded precursor polymers **10** with two different leaving groups. Treatment under thermal conditions led to a partially conjugated polymer **11** with regions of high and low HOMO–LUMO gap energy, showing a 30-fold improvement in electroluminescence efficiency compared with PPV, while treatment under acidic and thermal conditions gave more substantially conjugated polymers **12** with lower HOMO–LUMO gap energies. This chemistry enabled the formation of lithographically patterned polymers exhibiting electroluminescence. The scope of these copolymerizations was also explored with other copolymers, **19** and **22b,c**.

Introduction

The discovery that conjugated polymers can be utilized as the light-emitting layer in an electroluminescent (EL) polymer device has initiated investigations to gain control of the color and efficiencies of such materials.[1-9] There is clear evidence that excitons, formed from the capture of an electron and a hole, diffuse significant distances before decay. This gives them the chance to find quenching centers which allow nonradiative decay.[9,10] To confine charge in traditional inorganic semiconductor materials like GaAs, quantum wells are built into the device structure from growing layers of semiconductor with the middle layer having the lowest band-gap energy.[11] This technique can also be transferred to organic materials and conjugated polymers of different energy gaps by preparing multilayer devices.[10]

Exciton confinement can be achieved not only on a macroscopic scale with multilayer devices but also on a molecular scale within a polymer chain in a molecular quantum well, a local potential minimum. This necessitates the preparation of a polymer which has regions of high and low HOMO–LUMO gap energy. Poly(arylenevinylene)s and in particular the (co)polymers based on PPV have offered a unique opportunity to accomplish this in conjugated polymers.

Results and Discussion

Over the past few years we have been interested in the effect of the preparative route on the physical and electronic structure of PPV.[7,12-14] The understanding of substituents and their effects on the chemical reactivities of the various precursor homopolymers

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[†] University Chemical Laboratory.

[‡] Cavendish Laboratory.

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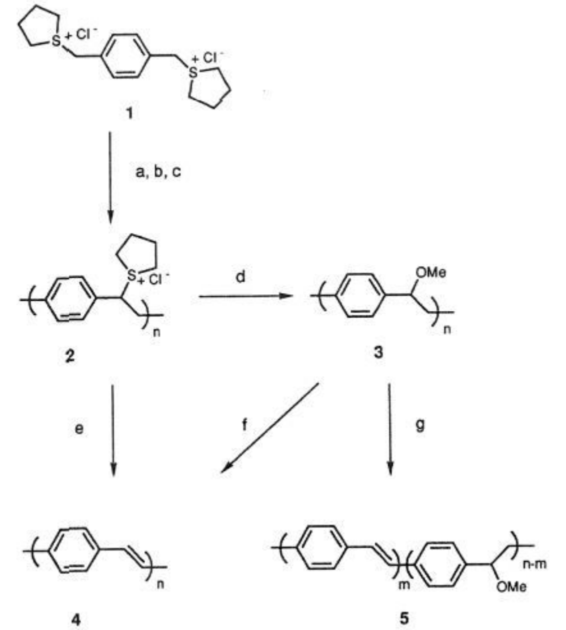
Scheme I[a]



[a] Key: (a) NaOH, MeOH/H_2O, 0 °C, 1 h; (b) HCl; (c) dialysis (water); (d) MeOH, 50 °C, 16 h; (e) 220 °C, vacuum, 2 h; (f) 220 °C, HCl(g)/Ar, 22 h; (g) 300 °C, vacuum, 12 h. The symbol n represents the polymerization degree and $m/(n-m)$ stands for the ratio of conjugated to nonconjugated segments.

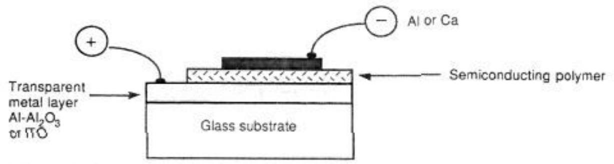
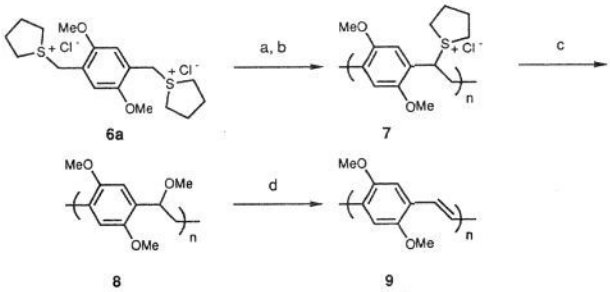


Figure 1. Construction of an ELPD. The precursor polymer was deposited (typical thickness *ca.* 100 nm) onto a substrate containing the anode (Al/Al_2O_3 or indium/tin oxide on glass) by spin coating from a solution in a suitable solvent. The film was thermally converted into the conjugated polymer. The cathode (Al or Ca) was deposited to a thickness of *ca.* 100 nm by vacuum evaporation (10^{-6} Torr).

Scheme II[a]



[a] Key: (a) $[Bu_4N]^+\ ^-OH$, MeOH, 0 °C, 2 h; (b) HCl, MeOH; (c) MeOH, 20 °C, 12 h; (d) 220 °C, HCl(g)/Ar, 22 h.

led us to utilize them in the design of copolymers. We envisaged two approaches, the first requiring the preparation of a precursor homopolymer which has a reasonably thermally stable leaving group. The second pathway demanded the preparation of precursor copolymers from more than one monomer.

The preparation of PPV **4** has previously been reported using either a sulfonium polyelectrolyte precursor polymer **2** or a methoxy leaving group precursor polymer **3**. The sulfonium route permits the removal of the labile sulfonium groups selectively by thermal treatment[12-17] while the elimination of methoxy groups requires both heat and acid treatment[7a,12,14a,18] (Scheme I). We have utilized this successfully to form a copolymer with regions of saturated and unsaturated units. Thin films (thickness 60–100 nm) of the methoxy precursor polymer **3** (Scheme I)[7a,12,14a,18] were treated at 300 °C for 12 h under vacuum. The UV/visible spectrum of the resultant polymer **5** indicated that the polymer contained conjugated sequences mainly comprising stilbene and distyrylbenzene units. The conjugation was interrupted by ethanediyl units which still had methoxy groups attached. The infrared spectrum of the thermally prepared polymer showed that there had been a decrease in the intensity of the methoxy group stretching mode (1097 cm^{-1}) with a concomitant increase in the absorption due to the vinylic out-of-plane deformation (965 cm^{-1}). We incorporated this copolymer as the light-emitting layer in an EL device using aluminum and indium/tin oxide as metal electrodes (see Figure 1).[7] The emission of the device under an applied bias indicated two features. The efficiency (measured as photons emitted per electron injected) was twice that of PPV in the same device configuration, either as a result of the increased fluorescence yield in the copolymer compared with PPV or because of the exciton confinement now occurring away from defect sites. The emission maximum (508 nm) was blue-shifted compared with that of PPV (551 nm), indicating that the average conjugated unit was shorter than that in PPV. The concept of modulating the conjugation length and enhancing EL efficiency by controlled elimination of poly(arylenevinylene) precursor polymers has subsequently been used with effect by other groups.[19]

The focus of our discussion of copolymers prepared from precursor copolymers centers on precursors to PPV and poly[(2,5-dialkoxy-*p*-phenylene)vinylene]s. It should be pointed out that the two homopolymers differ considerably in their optical properties. The HOMO–LUMO energy gap of poly[(2,5-dialkoxy-*p*-phenylene)vinylene]s is reduced by about 0.3 eV compared with that of PPV, which is also apparent in their color, the former being orange and the latter yellow. We have combined two important observations in the formation of these polymers. First, we have shown that the sulfonium precursor homopolymer to poly[(2,5-dimethoxy-*p*-phenylene)vinylene], PDMeOPV **7**, will react with methanol to form a methoxy leaving group precursor polymer **8** at room temperature (Scheme II) while, on the other hand, the sulfonium precursor polymer to PPV **2** requires heating to about 50 °C to achieve the corresponding conversion (Scheme I).[12,14a,18] Second, as already mentioned, the sulfonium group can be thermally eliminated to give conjugated units; removal of methoxy groups, however, requires not only heat but also acid catalysis for complete reaction.[12,14a,18]

The essence of our approach required the synthesis of a precursor polymer containing two different leaving groups such that the control of the conversion conditions would allow either preferential elimination of one of these groups to produce conjugated segments isolated by saturated units or elimination of both groups at the same time.

We synthesized a range of PPV/poly[(2,5-dialkoxy-*p*-phenylene)vinylene] statistical copolymers **11** and **12** via a solution-processible precursor polymer of form **10** as shown in Scheme

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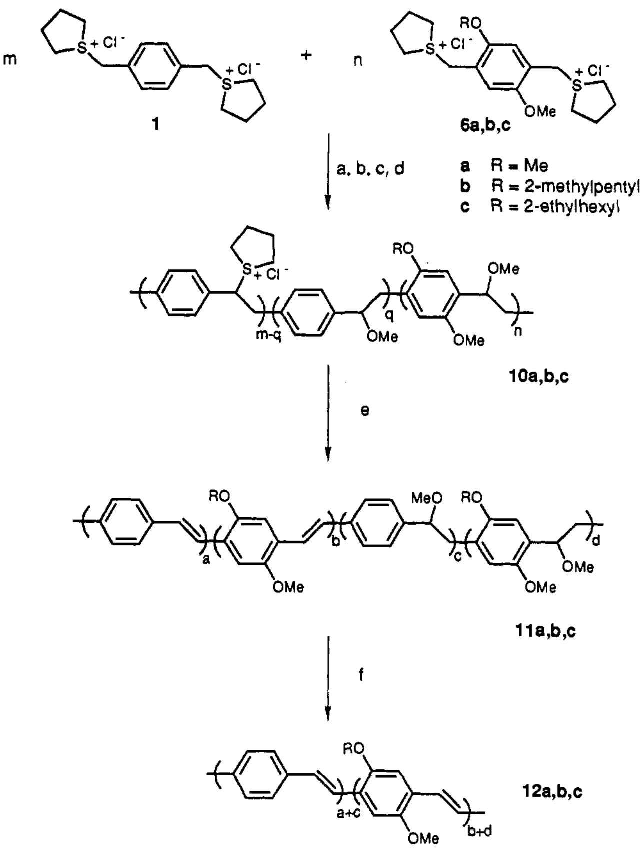
Scheme III[a]



[a] Key: (a) NaOH, H_2O/MeOH, 0 °C, 1 h; (b) HCl; (c) dialysis (water); (d) MeOH; (e) 220 °C, vacuum, 2 h; (f) 220 °C, HCl(g), 22 h. The symbols *m* and *n* represent the molar equivalents of monomeric bis(sulfonium) salts **1** and **6** in the feed mixture; *n* + *m* and *a* + *b* + *c* + *d* indicate the polymerization degree; *q* and *c* stand for a small number of benzylic positions adjacent to the phenylene units in **10** and **11** which have been substituted by methoxy groups.

III. The ratio of the units in the copolymer was controlled by using different feed ratios of the monomers **1** and **6**. The copolymerization of a methanolic solution of the two bis(sulfonium) salts at 0 °C was achieved with an equimolar quantity of aqueous sodium hydroxide. After termination of the polymerization with dilute hydrochloric acid and purification of the copolymer by dialysis against distilled water, the solvent was completely removed and the residue was redissolved in distilled methanol. This is the solvent of choice for preparing thin uniform films from sulfonium salt precursors.[1,14a] Using this procedure, we obtained a range of copolymers **10a** with monomer feed ratios of **1** and **6a** of 19:1, 9:1, 17:3, 4:1, and 7:3.

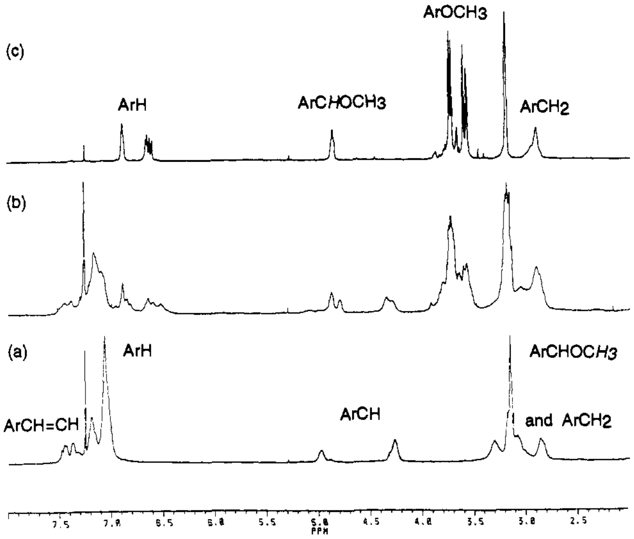
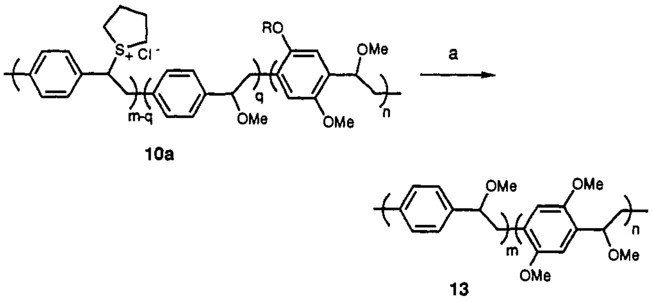


Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of (a) polymer **3**, (b) a copolymer **13** (obtained from a 4:1 feed ratio of monomers **1** and **6a**), and (c) polymer **8**.

Scheme IV[a]



[a] Key: (a) MeOH, 55 °C, 18 h.

Although copolymers of PPV **4** and PDMeOPV **9** have been prepared before by the copolymerization of bis(sulfonium) salts **1** and **6a** in *aqueous* solutions, they were formed from a precursor copolymer with just one leaving group, a tetrahydrothiophenium group.[15] When these precursor polymers were thermally converted in one step to **12a**, the HOMO–LUMO gap energy of the resultant conjugated copolymers was broadly independent of the ratio of the two monomer units used and was therefore similar in energy to PPV. By contrast, our materials were copolymerized in *water–methanol* solvent mixtures which allowed the reactions to be closely controlled. Direct comparison of the materials obtained by Lenz *et al.*[15] with the materials prepared by us showed that they were different for three important reasons. First, we noted the presence of both tetrahydrothiophenium and methoxy leaving groups in the precursor polymers. A very rough indication of the ratio of the two units incorporated is evident from IR (asymmetric C–O–C stretching frequency of the aromatic and benzylic methoxy groups) and ^{1}H NMR spectroscopy. As the signals in the ^{1}H NMR spectra of the sulfonium precursor polymers were broad,[12] we transformed the sulfonium precursor polymers **10a** to the corresponding methoxy leaving group precursors **13** (Scheme IV). By comparing the frequencies of the signals in the ^{1}H NMR spectra with those observed for the homopolymers,[12] it was possible to assign the signals due to the methine protons and aromatic protons (Figure 2). The integration ratio of the methine peaks indicated quite clearly that there was an increase of dimethoxyphenylene units incorporated into the precursor polymer when we used higher portions of **6a** in the monomer feed mixture. Second, the reaction rate of both monomers in the mixed solvent was faster compared to the rate with water alone as the solvent during polymerization. This is evidenced by the need for only a small amount of acid to neutralize the remaining unreacted base in the copolymerization procedure. Third, the copolymerization solvent permits selective substitution of the tetrahydrothiophenium group by methanol. This occurs at a faster rate at those benzylic carbons which are attached to an activated phenylene ring, in this case a dimethoxyphenylene ring. The observation that methanol is a better nucleophile than water had previously been observed in the preparation of the methoxy precursor to poly(2,5-thienylenevinylene).[18] Evidence for substitution in the copolymers arises from NMR and IR spectra. Although the signals in the ^{1}H NMR spectra of the sulfonium precursor polymers were broad and overlapping, it was possible to see that there was a decrease in the signals of the benzylic methine protons on carbons carrying sulfonium groups with a concomitant increase of signals which correspond to methine protons at the benzylic position to which a methoxy group was attached.

The incomplete elimination of the methoxy leaving group from copolymer precursors under the thermal conversion procedure

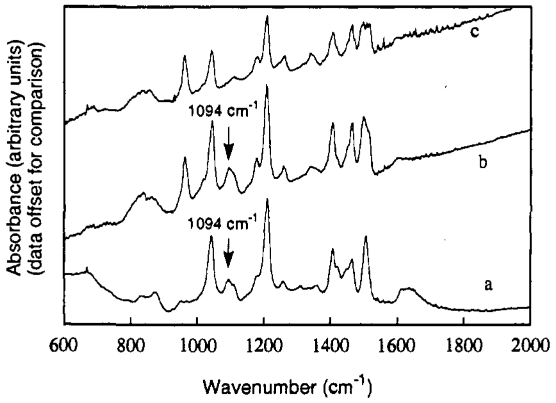


Figure 3. Infrared spectra of the copolymer prepared from a 4:1 feed ratio of **1** and **6a**: (a) precursor copolymer **10a** (free-cast film); (b) spin-coated film on KBr disk converted to **11a** at 220 °C *in vacuo* for 2 h; (c) same sample further converted to **12a** for 2 h in Ar/HCl at 220 °C.

utilized here is ascribable to the difficulty of elimination of the methoxy leaving group, as had previously been shown in analogous reactions with the homopolymers **3** and **8**.[12,14a,18] Infrared spectra of polymer **10a** showed an absorption at 1094 cm^{-1} (assigned to the asymmetric C–O–C stretching frequency in **8**[12,14a]) indicating that there was methoxy substitution next to the 2,5-dimethoxyphenylene units (Figure 3a). There was also a shoulder observed at 1097 cm^{-1}, which, by comparison with the infrared spectrum of **3**,[12,14a] indicated that some methoxy substitution next to phenylene units had also occurred.

Thermal conversion of spin-coated thin films (thickness *ca.* 100 nm) of polymers **10a** (220 °C for 2 h at 10^{-5} Torr) formed the polymers **11a**, which were found to be homogeneous, dense, and uniform. Infrared spectroscopy of polymers **11a** (Figure 3b) showed that there were still methoxy leaving groups present after the thermal treatment and, thus, that the product consisted of a statistical assembly of discrete conjugated segments separated by saturated units. The UV/visible spectra confirmed that purely thermal treatment yielded polymers **11a** consisting of conjugated and nonconjugated segments, with more nonconjugated moieties for higher proportions of 2,5-dimethoxyphenylene monomer **6a** in the monomer feed mixture. Thin films of **11a** prepared by this method were stable to the loss of the methoxy groups; *e.g.*, films heated for 2 h had properties similar to those of films heated for 24 h, as evidenced by IR and UV/visible spectroscopy. Polymers **10a** required thermal treatment under acidic conditions (220 °C, HCl(g)/Ar, 22 h) to form the more conjugated polymers **12a**. These conditions (even after initial thermal treatment) are insufficient for the complete elimination of all the methoxy groups which disrupt the conjugation. This was observed by both infrared spectroscopy [after 2 h the intensity of the IR band at 1097 cm^{-1} was reduced by a factor of about 10 (Figure 3c)] and UV/visible spectroscopy (Figure 4). For the combined thermal and acid treatment, the HOMO–LUMO energy gap of the polymers **12a** was still greater than that of PPV except for the copolymer prepared from a 4:1 feed ratio of **1** to **6a**, although the polymers containing a greater proportion of dimethoxyphenylene units displayed a stronger red shift in energy gap. Presumably, under these conditions the hydrogen chloride cannot penetrate fully into the film to achieve full conversion to conjugated units, or elimination is conformationally restricted.[7a,14b]

It should be noted that the elimination of sulfonium groups from **10a** to form vinylene units involves the liberation of hydrogen chloride as one of the byproducts. Hydrogen chloride is also the reagent required to catalyze removal of methoxy leaving groups. Therefore the possibility arises to use this reagent for selective elimination reactions in the copolymer. The thin copolymer film samples lose the acid too rapidly for this effect to be utilized. In thick-film samples prepared by static solution casting, however, the extent of conversion is significantly enhanced. This is clearly evidenced in their color (they are unfortunately too thick for optical absorption measurements), which, unlike that of the uniformly yellow thin-film samples, becomes increasingly red as the content of dimethoxyphenylene units in the copolymers increases. It is also indicated by the decrease of the strength of the characteristic C–O–C stretching frequency in the IR spectra that is associated with the methoxy modifier group on the benzylic carbon. This behavior can be understood as being due to the lower rate of loss of acid from the bulk of thick films, greater interaction with the units of the methoxy precursors and consequently leading to further conversion. Alternatively, converting a spin-coated copolymer **10a** film [prepared from **1** and **6a** (17:3)] on a glass substrate initially with a low-temperature bake *in vacuo* at about 100 °C sufficiently reduces the diffusion rate of the acid out of the film to give an enhanced probability of causing elimination of methoxy pendant groups. A subsequent bake at 220 °C *in vacuo* results in a considerable reduction in the energy gap obtained (by about 0.14 eV) over material heated directly to 220 °C *in vacuo*.

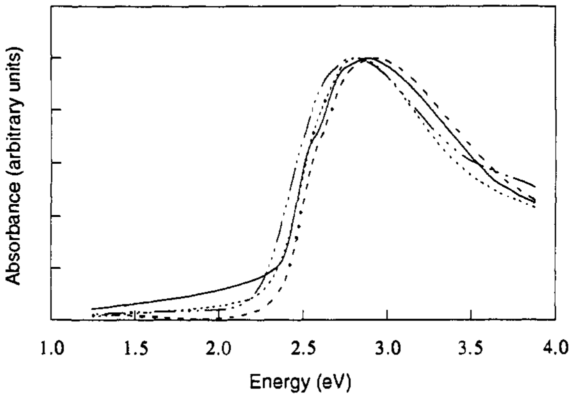


Figure 4. UV/visible absorption spectra of PPV (—) and the copolymers **12a** prepared from monomers **1** and **6a** in the ratios 9:1 (– –), 17:3 (- - -), and 4:1 (— - - -).

We have extended the scope of the chemistry developed here to produce *two colors* within a single film.[5] An aluminum mask was deposited on the precursor copolymer surface according to a predefined lithographic pattern. The aluminum cap provides a physical barrier to the hydrogen chloride, which promotes formation of more conjugated polymers. After etch-removal of the metal mask, the polymer underneath showed a deeper orange appearance to the eye and a striking difference in refractive index.[5] These differences are also evidenced in the absorption and photoluminescence spectra of the two regions within the same copolymer film (Figure 5). A two-color-patterned copolymer film [prepared from **1** and **6a** (9:1), thickness 1500 Å] was fabricated as an electroluminescent device (see Figure 1) with indium/tin oxide hole-injecting and calcium electron-injecting contacts. The latter was deposited over the whole device after patterning of the polymer and etch-removal of the aluminum overlayer. When the device was driven in forward bias (ITO positive), emission was observed for voltages about above 10 V. Emission was observed from the partially conjugated regions, corresponding to polymers of structure **11a**. This observation is consistent with the observation (see below) that the partially conjugated material has a higher quantum efficiency for electroluminescence, and it demonstrates the ability to produce passive emissive elements by a negative lithography process.

We have developed a family of copolymers in which the conjugation length can be controlled by varying the conversion conditions of the precursor polymers having two different types of leaving groups. This in turn controls the color of the emitted light. For purely thermal conversion there was an incomplete elimination in thin films such that the resultant conjugated segments were separated by residual nonconjugated units, causing the energy gap to increase relative to that of PPV. For acid-

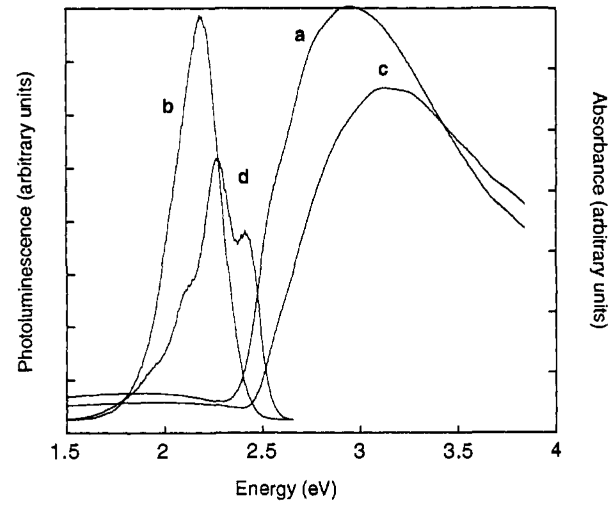
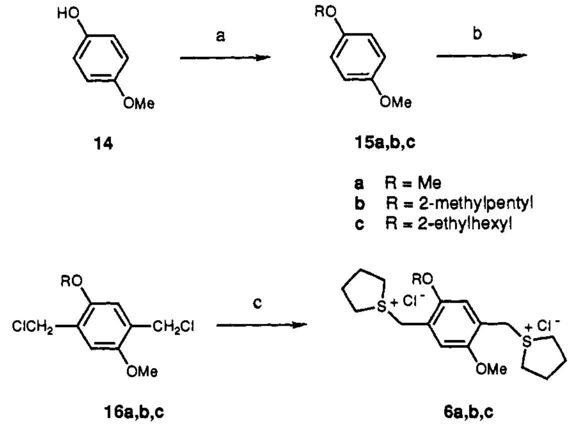


Figure 5. Absorption (a) and photoluminescence (b) spectra of a capped (polymer **12a**) sample and absorption (c) and photoluminescence (d) spectra of an uncapped (polymer **11a**) sample of copolymer made from a 9:1 feed mixture of **1** and **6a**.

catalyzed thermal conversion of thin films, or for thermal treatment of thick films, the elimination is more substantial, with the result that the absorption shifts to the red. The gradation in color shift, according to the relative proportions of dimethoxyphenylene to phenylene unit, is indicative that the polymer is formed in a statistical manner; significant changes in color would not be expected for a block copolymer formed initially from the more reactive dimethoxyphenylene units and subsequently from phenylene units.

Inclusion of polymers **11a** between aluminum oxide and aluminum electrode contacts in an EL device showed a maximum efficiency (photons out/electrons in) of 0.3% for the copolymer prepared from monomers **1** and **6a** in a feed ratio of 9:1.[5a] This considerable improvement in the electroluminescent device efficiency was achieved with copolymers of PPV and PDMeOPV, even though the photoluminescence yield for PDMeOPV is 20–30 times less than that for PPV.[9] Poly[(2,5-dialkoxy-*p*-phenylene)vinylene]s with disruption of the packing of the polymer chains by long alkoxy substituents not only are soluble in organic solvents but also show higher photoluminescence yields than PDMeOPV.[20] This has been observed for, *e.g.*, poly[(2,5-bis(heptyloxy)-*p*-phenylene)vinylene][2] and poly[(2-((2-ethylhexyl)oxy)-5-methoxy-*p*-phenylene)vinylene], MEH-PPV.[21] We wished to know whether this was a general phenomenon for all poly[(2,5-dialkoxy-*p*-phenylene)vinylene]s, and the logical choice to test this hypothesis was a copolymer based on either MEH-PPV or an analogue. We chose a derivative of monomer **6a** where one of the two methoxy groups had been replaced by a branched (2-methylpentyl)oxy or (2-ethylhexyl)oxy side chain, the latter being known from MEH-PPV.[21] The preparation of the bis(sulfonium) salt **6b** (Scheme V) followed essentially Wudl's procedure for **6c**.[21] 4-Methoxyphenol (**14**) was alkylated with 1-bromo-2-methylpentane or 3-(bromomethyl)heptane, respectively. The resulting **15b,c** were then chloromethylated to give **16b,c**. Reaction with tetrahydrothiophene furnished the required monomers **6b,c**. Copolymerizations of **1** and **6b,c** (19:1, 9:1, 4:1) were conducted as shown in Scheme III. As observed for **11a**, the data for **11b,c** (from a 19:1 and 9:1 monomer feed ratio) are consistent with incomplete conversion of the precursor units during the thermal treatment. However, the thermally converted copolymers **11b,c** (obtained from a 4:1 mixture of **1** and **6b,c**) exhibited an absorption maximum between those of PPV and **11b,c** (from a 19:1 monomer feed ratio), as shown in Figure 6. It is possible that the different behavior of **11b,c** compared with **11a** might be due to differences in the reactivity of benzylic leaving groups in the presence of long solubilizing alkoxy side chains. The performance of copolymers **11b,c** in an EL device (device configuration as for **11a**) was at least as good as that of PPV yet surprisingly inferior to that of **11a**. The copolymer **11b**, prepared from a **1**:**6b** monomer feed ratio of 9:1, showed a maximum efficiency in an EL device of only about 15-fold that of PPV.

Scheme V[a]



[a] Key: (a) RBr, KOH, EtOH, reflux, 16 h; (b) HCl (37%), formaldehyde (39%), dioxane, 20 °C, 18 h, reflux, 4 h; (c) tetrahydrothiophene, MeOH, 50 °C, 17 h.

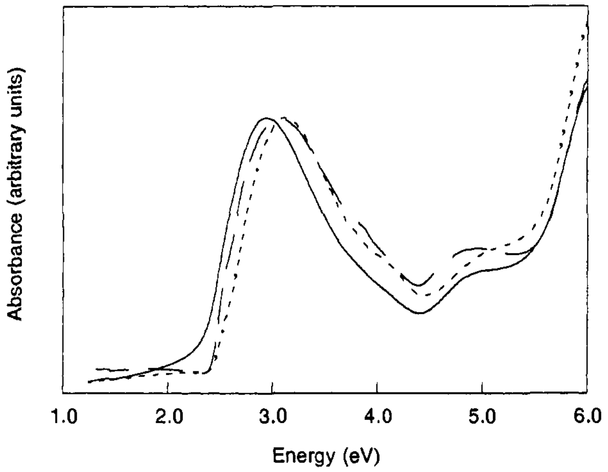


Figure 6. Absorption spectra of copolymers **12b** obtained from 19:1 (— —), 9:1 (- - -), and 4:1 (—) feed ratios of monomers **1** and **6b**.

Poly[(2,5-dimethyl-*p*-phenylene)vinylene] has a higher HOMO–LUMO energy gap than does PPV owing to the steric inhibition of planarity arising from allylic strain caused by the aromatic methyl substituents.[22] On the other hand, the reactivity of the precursors to poly[(2,5-dimethyl-*p*-phenylene)vinylene] is intermediate between those for PPV and PDMeOPV, as expected on electronic grounds (the two methyl groups on the aromatic ring are inductively electron-donating).[12] As outlined in Scheme VI, we prepared a number of copolymers from **1** and **17** (monomer feed ratios 19:1, 9:1, 4:1). Spin-coated films (60–100 nm thick) of copolymers **18** were thermally converted (220 °C for 12 h at 10^{-5} Torr). The resulting polymers **19** showed a shift in the position of the absorption peak to higher energy compared to that seen for PPV; for example, the copolymer **19**, prepared from a 9:1 mixture of **1** and **17**, showed an increase in energy at the peak in absorption of 0.12 eV. There are two possible explanations for the observed higher HOMO–LUMO gap energy. The conju-

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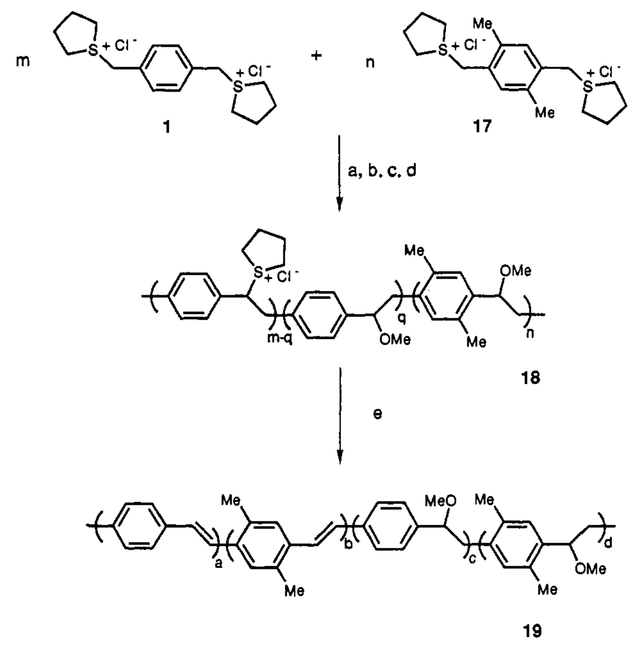
(20) High luminescence quantum efficiency was recently reported for xylene solutions of MEH-PPV: Moses, D. *Appl. Phys. Lett.* **1992**, *60*, 3215–3216.

(21) Wudl, F.; Allemand, P. M.; Srdanov, G.; Ni, Z.; McBranch, D. *ACS Symp. Ser.* **1991**, *455*, 683–686.

(22) (a) Lhost, O.; Brédas, J. L. *J. Chem. Phys.* **1992**, *96*, 5279–5288. (b) Martens, J. H. F.; Marseglia, E. A.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Synth. Met.* **1993**, *55–57*, 449–453.

Scheme VI[a]



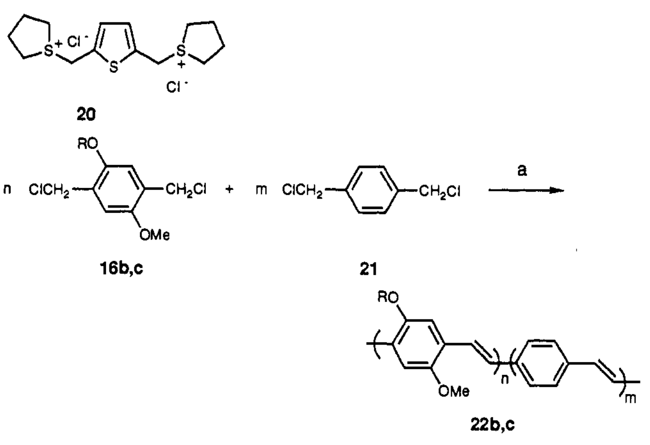
[a] Key: (a) NaOH, H_2O/MeOH, 0 °C, 1 h; (b) HCl; (c) dialysis (water); (d) MeOH; (e) 220 °C, vacuum, 2 h. For the definition of *a*, *b*, *c*, *d*, *m*, *n*, and *q*, see Scheme III.

gation may be disrupted by twisting to avoid allylic strain between the methyl substituents and the vinylidene groups.[12] In addition, the methoxy pendant groups may not be been fully eliminated, thus resulting in a copolymer structure containing conjugated and nonconjugated segments. In an EL device with a configuration of aluminum oxide/polymer/aluminum, the copolymer **19** did not show a significant enhancement in device efficiency over PPV.[9]

Copolymers[23] prepared from **1** and thiophene-derived bis(sulfonium) salt monomer **20** (monomer feed ratios 19:1, 9:1) did not give rise to any improvement in electroluminescent properties over PPV itself. Furthermore, the difference in reactivity between the two monomers made it difficult to control the composition of the desired copolymers.

We further investigated a range of conjugated copolymers which can be processed from solution. Scheme VII outlines their preparation from bis(chloromethyl) compound **16b** or **16c** and α,α'-dichloro-*p*-xylene (**21**) (monomer feed ratios 19:1, 9:1, 4:1) using excess potassium *tert*-butoxide to induce polymerization and conversion of the intermediate chloro precursor to the fully conjugated copolymers **22b,c**. Chloroform- and tetrahydrofuran-soluble polymeric material could be obtained with ratios of **16b,c** to **21** greater than 7:3. The absorption spectra of the new copolymers **22b,c** and the respective homopolymer poly[(2-methoxy-5-((2-methylpentyl)oxy)-*p*-phenylene)vinylene], or MEH-PPV, were similar in onset and appearance, although the corresponding photoluminescence and electroluminescence spectra indicated a minor trend to higher energy with increasing number of unsubstituted phenylenevinylidene units. We used these copolymers in the fabrication of a number of EL devices. In an ITO/polymer/Ca device configuration, the polymers **22b,c** exhibited device efficiencies comparable to those of the corresponding homopolymers.

Scheme VII[a]



b R = 2-methylpentyl
c R = 2-ethylhexyl

[a] Key: (a) KOtBu, THF, 20 °C, 22 h.

Conclusion

We have outlined the scope and the advantages of copolymers related to PPV and MEH-PPV, two conjugated poly(arylenevinylene)s which recently found considerable interest as light-emitting materials in electroluminescent devices. Some of the copolymers prepared (**12** and **22**) were substantially fully conjugated, but the majority owed their properties to the fact that they consisted of intermittent sequences of conjugated and nonconjugated segments. Their synthesis was achieved by deliberate use of methoxy leaving groups in precursor polymers which mainly withstood elimination upon heating to 220 °C. We have further demonstrated that statistical precursor copolymers with two different leaving groups, *viz.* benzylic methoxy and sulfonium pendant groups, can be selectively converted to cause elimination of either the sulfonium groups alone (heat treatment) or both leaving groups (simultaneous head and acid treatment) by choice of the reaction conditions. As expected, copolymers **11a** and **12a** showed significant differences in their absorption spectra. The presence of methoxy groups in **10a** and **11a** gave rise to a characteristic C–O–C stretching frequency in the infrared spectra. A similar behavior was noticed for other copolymers (**11b,c** and **18**). Copolymers **11a** proved to be the most versatile because they exhibited the highest efficiency in EL devices compared with the other materials described in this paper. It was also possible to obtain copolymers **11a** and **12a** as separate regions within the same copolymer film by applying a specially designed patterning procedure on the precursor copolymer **10a**.

Experimental Section

General Methods. Methanol was dried and purified by distillation from magnesium methoxide.[24] Distilled water was used in the reactions, and the aqueous sodium hydroxide and hydrochloric acid solutions were freshly prepared for each reaction. Bis(sulfonium) salt monomers **1**,[15b] **6a**,[15b] **17**,[12] and **20**[25] were prepared according to literature procedures. All polymerizations were carried out under nitrogen or argon. For dialysis, a cellulose membrane dialysis tubing with a molecular mass cutoff of 12 400 Da (supplied by Sigma Chemical Co. Limited, Dorset, U.K.) was used. ^1H NMR spectra were recorded on a Bruker WM-400 or AC-250 spectrometer with tetramethylsilane as internal reference. ^{13}C NMR spectra were recorded on a Bruker WM-400 spectrometer. Infrared spectra of polymers were recorded on a Nicolet 5SXB FTIR spectrometer either as free standing films or as films on pressed potassium bromide disks. UV/visible spectra were recorded as spun films on either glass or Spectrosil substrates on a Perkin-Elmer Lambda 9. Spin-coated samples were typically prepared by covering a substrate with a solution of the precursor polymer and spinning at 2000 rpm for 60 s on a Dynapert PRS14E spin-coater for photoresists, allowing the solvent to evaporate under ambient conditions. The precursor films (spun or free-cast) were

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(23) Copolymers of this type have been reported by: (a) Jin, J.-I.; Shim, H.-K.; Lenz, R. W. *Synth. Met.* **1989**, *29*, E53–E60. (b) Shim, H.-K.; Lenz, R. W.; Jin, J.-I. *Makromol. Chem.* **1989**, *190*, 389–397. (c) Gregorius, R. M.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1992**, *25*, 6664–6669.

(24) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Harlow, U. K., 1989; p 400.

(25) Han, C.-C.; Jen, K.-Y. A.; Elsenbaumer, R. L. (Allied-Signal Inc.) U.S. Pat. 4,900,782, Feb 13, 1990; *Chem. Abstr.* **1990**, *113*, 7051c.

converted to conjugated materials either by thermal treatment under a dynamic vacuum or by thermal treatment under a constant flow of a mixture of hydrogen chloride and argon. The thicknesses of films produced by spin-coating were in the range of 60–100 nm after conversion from the precursor polymers. Such films provided optical densities at the peak of the π–π^* absorption maximum in the range 1–3. Gel permeation chromatography (GPC) separations of methoxy-substituted precursor polymers were carried out with a Polymer Laboratories PLgel 5-μm MIXED-C column (300-mm length) calibrated with polystyrene narrow standards (mass range 1 130 000–580 Da) in chloroform with toluene as flow marker. The chloroform solvent was pumped at 7 MPa at a flow rate of 10 mL min^{-1} at 30 °C, and the UV detector was set at 310 nm. Melting points were determined using a Büchi 510 melting point apparatus. Microanalyses were determined by Mr. D. Flory and staff at the University Chemical Laboratory. Mass spectra were carried out by Dr. J. A. Ballantine and colleagues at the SERC Mass Spectrometry Service, University College of Swansea.

All copolymers obtained via a sulfonium precursor route were prepared under the conditions shown in the following example.

Poly[*p*-phenylenevinylene-*stat*-(2,5-dimethoxy-*p*-phenylene)vinylene] (9:1). To a deoxygenated solution of **1** (0.97 g, 2.8 mmol) and **6a** (0.12 g, 0.30 mmol) in methanol (7.1 mL) cooled in an ice bath was added dropwise an ice-cold aqueous sodium hydroxide solution (0.4 M, 7.1 mL) over 10 min. The reaction mixture was stirred for 1 h at 0 °C under Ar and neutralized with hydrochloric acid (0.4 M, 1.0 mL). The solution was then dialyzed against water over 3 days (3 × 1000 mL), after which the solvent was completely removed. The residue was redissolved in methanol (15 mL). Thin films (of the order of 100 nm as used in EL polymer devices) of the copolymer **10a** could be obtained by spin-coating the precursor polymer solution. Thermal conversion of the said films were typically at 220 °C for 2 h. Alternatively, the spin-coated films were converted at 220 °C over 2 h in an argon flow which had been passed through concentrated hydrochloric acid.

A sample of the copolymer **10a** was further assayed by conversion into the fully methoxy-substituted material **13** by digestion in methanol at 55 °C for 18 h. The pale green precipitate was collected by suction filtration, washed with methanol, and dried. GPC assay revealed M_n 1.37 × 10^4, M_{peak} 6.26 × 10^4, M_w 1.34 × 10^5, and polydispersity index 9.8.

1-Methoxy-4-((2-methylpentyl)oxy)benzene (15b). Sodium metal (6.4 g, 280 mmol) was dissolved in dry methanol (100 mL) under Ar to give a 2.8 M solution of sodium methoxide. 4-Methoxyphenol (29.3 g, 235 mmol) and 1-bromo-2-methylpentane[26] (46.9 g, 284 mmol) were added, and the mixture was then heated to reflux for 2 days. After the reaction mixture was cooled to room temperature, ether (100 mL) and aqueous sodium hydroxide (0.5 M, 100 mL) were added. The organic layer was separated from the mixture, washed with water (2 × 100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Distillation of the crude product afforded **15b** (30.8 g, 63%): bp 104–105 °C/0.3 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.94 (3 H, t, J = 7.0 Hz), 1.02 (3 H, d, J = 6.7 Hz), 1.16–1.56 (4 H, m), 1.93 (1 H, m), 3.64–3.82 (2 H, m), 3.77 (3 H, s), 6.81–6.89 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 14.3, 17.0, 20.1, 33.0, 35.8, 55.7, 73.9, 114.6, 115.4, 153.5, 153.6; IR (film) ν_{max} 2956 (m), 1509 (s), 1232 (s), 1045 (m), 824 (m) cm^{-1}; MS (all *m/z*) 208 (M^+, 100), 124 (32); MS (high resolution) calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1463. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.03; H, 9.70.

1,4-Bis(chloromethyl)-2-methoxy-5-((2-methylpentyl)oxy)benzene (16b). A mixture of hydrochloric acid (37%, 59 mL), formaldehyde (39%, 35 mL), **15b** (14.0 g, 67.4 mmol), and dioxane (100 mL) was saturated with hydrogen chloride for 15 min at 0 °C and stirred for 1.5 h at room temperature. Another 30 mL of formaldehyde was then added at 0 °C, and hydrogen chloride was bubbled through the reaction mixture for 10 min. After 17 h of stirring at room temperature, the mixture was heated to reflux for 4 h. The solvents were then completely removed to give a colorless solid residue, which was dissolved in a minimum amount of hot hexane (50 mL). This solution was poured into ice-cold methanol (300 mL) and filtered under suction. The precipitate was dried to afford **16b** (15.5 g, 75%): mp 86–88 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.92 (3 H, t, J = 6.9 Hz), 1.04 (3 H, d, J = 6.8 Hz), 1.22–1.55 (4 H, m), 1.95–2.05 (1 H, m), 3.73–3.90 (2 H, m), 3.85 (3 H, s), 4.62 (2 H, s), 4.64 (2 H, s), 6.89 (1 H, s), 6.92 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.3, 17.1, 20.0, 35.7, 33.0, 41.3, 41.4, 56.3, 73.9, 113.3, 114.1, 126.8, 127.0, 150.8, 150.9; IR (KBr) ν_{max} 2958 (m), 1517 (s), 1466 (m), 1414 (s), 1263 (s), 1230 (s), 1036 (s), 734 (s), 696 (s) cm^{-1}; MS 304 (M^+, 18), 220 (38), 84 (41); MS (high resolution) calcd for $C_{15}H_{22}{}^{35}Cl_2O_2$ 304.0997, found 304.0997. Anal. Calcd for $C_{15}H_{22}Cl_2O_2$: C, 59.02; H, 7.27; Cl, 23.23. Found: C, 59.10; H, 7.36; Cl, 23.17.

1,1′-[(2-Methoxy-5-((2-methylpentyl)oxy)-*p*-phenylene)bis(methylene)]bis[tetrahydrothiophenium] Dichloride (6b). Tetrahydrothiophene (20.9 mL, 237 mmol) was added to a suspension of **16b** (14.5 g, 47.3 mmol) in dry methanol (200 mL). The solid dissolved to form a clear solution within 10 min. This solution was then heated to 50 °C for 17 h. The solvent was completely removed *in vacuo* and the residue poured into dry acetone. The solution was then filtered under suction and dried to give **6b** (12.7 g, 56%) as a colorless, hygroscopic solid: ^{1}H NMR (250 MHz, CD_3OD) δ 0.97 (3 H, t, J = 6.9 Hz), 1.10 (3 H, d, J = 6.8 Hz), 1.26–1.61 (4 H, m), 2.04 (1 H, m), 2.23–2.53 (8 H, m), 3.55 (8 H, m), 3.86–4.05 (2 H, m), 3.97 (3 H, s), 4.56 (2 H, s), 4.57 (2 H, s), 7.35 (1 H, s), 7.37 (1 H, s); ^{13}C NMR (CD_3OD) δ 14.7, 17.5, 21.1, 29.7, 29.8, 34.3, 36.9, 43.1, 43.2, 44.5, 44.6, 44.8, 57.1, 75.8, 116.5, 117.3, 121.3, 121.6, 153.0, 153.5; IR (KBr) ν_{max} 2953 (s), 1514 (s), 1404 (s), 1230 (s), 1033 (s) cm^{-1}. The sulfonium salts are hygroscopic, and it was difficult to obtain reliable and reproducible microanalytical data.

1-((2-Ethylhexyl)oxy)-4-methoxybenzene (15c) was synthesized by an adapted literature procedure.[21] Sodium metal (6.50 g, 283 mmol) was dissolved in dry methanol (100 mL) under Ar to give a 2.5 M solution of sodium methoxide. A solution of 4-methoxyphenol (29.3 g, 236 mmol) in dry methanol (150 mL) was added, and this mixture was heated to reflux for 30 min. After the reaction mixture was cooled to room temperature, a solution of 3-(bromomethyl)heptane[27] (46.5 g, 259 mmol) in dry methanol (150 mL) was added dropwise. The mixture was then heated to reflux for 18 h. The solvent was removed *in vacuo*, the residue was dissolved in ether (200 mL), and the ether solution was washed with dilute aqueous sodium hydroxide (500 mL) and water (500 mL), dried over $MgSO_4$, and concentrated *in vacuo* again. Distillation at 120 °C/0.1 Torr afforded **15c** (24.2 g, 43%): ^{1}H NMR (250 MHz, CD_3OD) δ 0.89–1.04 (m), 1.18 (3 H, t, J = 7.0 Hz), 1.29–1.65 (8 H, m), 1.82 (1 H, m), 2.32–2.55 (8 H, m), 3.50–3.65 (8 H, m), 3.90–4.05 (2 H, AB), 3.96 (3 H, s), 4.56 (2 H, s), 4.57 (2 H, s), 7.38 (1 H, s), 7.39 (s, 1 H); IR (KBr) ν_{max} 1508 (s), 1232 (s), 1045 (s), 824 (m) cm^{-1}.

1,4-Bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (16c) was synthesized by an adapted literature procedure.[21] A mixture of hydrochloric acid (37%, 90 mL), formaldehyde (39%, 70 mL), **15c** (24.2 g, 101 mmol), and dioxane (120 mL) was saturated with hydrogen chloride for 20 min at 0 °C and stirred for 3 h at room temperature. Another 50 mL of formaldehyde was then added at 0 °C, and hydrogen chloride was bubbled through the mixture for 10 min. After being stirred for 3 days at room temperature, the mixture was heated to reflux for 3.5 h. The solvents were then completely removed to give a pale yellow solid residue which was dissolved in a minimum amount of hot hexane (75 mL). This solution was poured into ice-cold methanol (300 mL) and filtered under suction. The precipitate was washed with methanol (200 mL) and dried to afford **16c** (27.2 g, 79%): mp 58–60 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85–0.96 (6 H, m), 1.26–1.75 (9 H, m), 3.74–3.86 (2 H, m), 3.83 (3 H, s), 4.06 (4 H, s), 6.89 (1 H, s), 6.90 (1 H, s); IR (KBr) ν_{max} 2924 (m), 1516 (s), 1466 (m), 1415 (s), 1263 (s), 1227 (s), 1182 (m), 1032 (s), 733 (m), 700 (s), 614 (m) cm^{-1}.

1,1′-[(2-((2-Ethylhexyl)oxy)-5-methoxy-*p*-phenylene)bis(methylene)]-bis[tetrahydrothiophenium] dichloride (6c) was synthesized by an adapted literature procedure.[21] Tetrahydrothiophene (6.4 mL, 72 mmol) was added to a suspension of **16c** (4.80 g, 14.4 mmol) in dry methanol (75 mL). The mixture was then heated to 50 °C for 22 h. The solvent was completely removed *in vacuo* and the residue treated with dry acetone. The solution was then filtered under suction and dried to give **6c** (4.36 g, 59%): ^{1}H NMR (250 MHz, CD_3OD) δ 0.89–1.04 (6 H, m), 1.18 (3 H, t, J = 7.0 Hz), 1.29–1.65 (8 H, m), 1.82 (1 H, m), 2.32–2.55 (8 H, m), 3.50–3.65 (8 H, m), 3.90–4.05 (2 H, m), 3.96 (3 H, s), 4.56 (2 H, s), 4.57 (2 H, s), 7.38 (1 H, s), 7.39 (1 H, s); IR (KBr) ν_{max} 2948 (br, m), 1514 (s), 1460 (m), 1399 (s), 1312 (m), 1229 (s), 1033 (s), 703 (m) cm^{-1}.

All soluble copolymers were prepared under the conditions shown in the following example.

Poly[(2-methoxy-5-((2-methylpentyl)oxy)-*p*-phenylene)vinylene-*stat*-*p*-phenylenevinylene] (9:1). A solution of **16b** (0.95 g, 2.90 mmol) and α,α'-dichloro-*p*-xylene (**21**) (50 mg, 0.29 mmol) in tetrahydrofuran (20

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[26] Rehberg, C. E.; Henze, H. R. *J. Am. Chem. Soc.* **1941**, *63*, 2785–2789.

[27] Shonle, H. A.; Waldo, J. H.; Keltch, A. K.; Coles, H. W. *J. Am. Chem. Soc.* **1936**, *58*, 585–587.

mL) was added to a solution of potassium *tert*-butoxide (95%, 2.5 g, 22 mmol) in tetrahydrofuran (120 mL) over 15 min. The mixture was then stirred at room temperature for 22 h. The resulting orange mixture was reduced to 10% of its volume and poured into methanol (500 mL). The precipitate was filtered out under suction and reprecipitated from tetrahydrofuran/methanol to afford 101 mg of polymer **21b**.

Acknowledgment. We thank the SERC for supporting this work and Cambridge Research and Innovation Limited and Pfizer Central Research for partial financial support. Christ's College, Cambridge, provided a Dow Research Fellowship (P.L.B.), and the Deutsche Forschungsgemeinschaft provided a fellowship (A.K.). We are grateful to Dr. A. Griffin and Mr. G. J. Sarnecki for generous assistance with the gel permeation chromatography separations.

Supplementary Material Available: Figures 7–9, showing photoluminescence and electroluminescence spectra of copolymer **5**, absorption spectra of copolymers prepared from **1** and **6a**, and absorption spectra of MEH-PPV and copolymers **22c** (2 pages). Ordering information is given on any current masthead page.