

The preparation and some properties of substituted phenylene-ethynylene and phenylenebuta-1,3-diynylene polymers

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Syntheses are described for the preparation of a variety of diynes which are converted to high molecular weight substituted arylenebuta-1,3-diynylene polymers by oxidative coupling and to high molecular weight substituted arylene-ethynylene polymers by Pd(II) catalysed cross coupling reactions. The products tend to be insoluble in normal organic solvents. Doping with ferric chloride produces significant changes in conductivity but these are less than those produced on equivalently substituted thienylene-phenylene polymers.

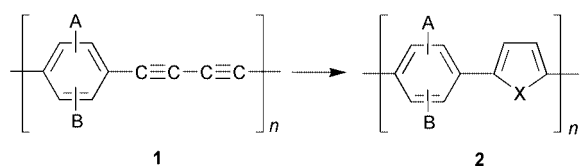
Introduction

Since the discovery that films of polyacetylene can be made electrically conducting^{1,2} much effort has been directed to the design, synthesis and application of novel organic materials which combine the desirable material properties of conventional synthetic polymers with the electrical properties of metals. This active interest is reflected in the hundreds of research reports that appear annually as well as in a variety of review articles^{3,4} and books.^{5,6}

Our interest in this area began^{7,8} with the realisation that the then available methods for the chemical and electrochemical preparation of conjugated polymers resulted in some degree of randomisation in the unit linkages.^{9–11} Thus methodology was required that would allow complete control of regiochemistry and be versatile enough to allow synthesis of a large number of structures so that structure–property relationships could be defined. We introduced such a methodology based on transition metal catalysed cross coupling of arylene dihalides with variously metallated heteroaryls^{7,8} and recently reported our results on the synthesis of substituted phenylene–thiophenylene oligomers and polymers.¹²

Despite the success of this methodology for the control of regiochemistry and the introduction of substituents, only low molecular weights of *ca.* 3000–10000 were obtained.^{12,13} It is generally agreed¹⁴ that oligomers/polymers of this kind of molecular weight cannot achieve the mechanical strength required to make films and fibres. Indeed as a single cross-coupling reaction proceeds in only 70–90% yield Caruther's equation¹⁵ indicates that this methodology *cannot* yield high molecular weight polymers.

A new approach was required and we chose to examine the synthesis and properties of poly(arylenebuta-1,3-diynylene)s **1**. This decision was based on the known cyclisations of buta-1,3-diynes to yield heteroaromatics.^{16–21} The extension of this methodology to the preparation of poly(heteroarylene-phenylene)s **2** can be readily envisaged (Scheme 1) as long as the necessary precursor polymers **1** are available.



Scheme 1

Thus if high molecular weight polymers **1** could be prepared in a regiospecific fashion not only might they yield the polymers **2** but their own electrical properties would also be of great interest.

Acetylenic polymers

Only wholly organic systems and not metal containing acetylenic polymers^{22–30} will be considered here. 1,4- and 1,3-Diethynylbenzenes have been polymerized to give phenylenebuta-1,3-diynylene polymers with average molecular weights of between 8700 to 30000.^{31–33} Thienylenebuta-1,3-diynylene polymers have recently been synthesised in an analogous fashion.³⁴

Palladium catalysed cross coupling reactions have been used to build phenylene-ethynylene polymers^{35–38} but molecular weights were only in the region of 1500–5000.

Results and discussion

1. General considerations

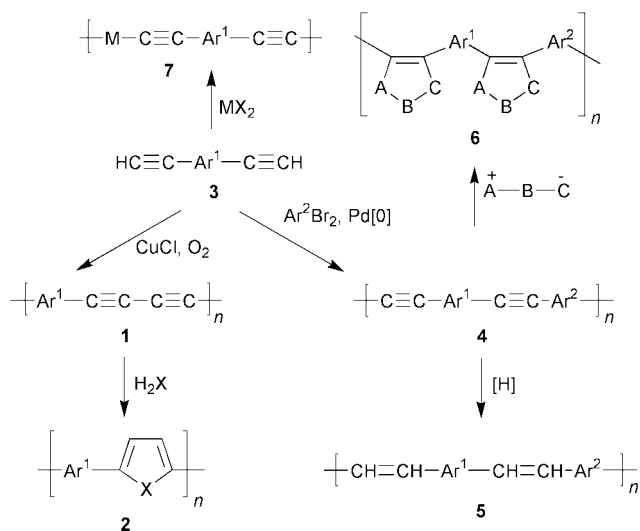
We realised that high molecular weight, substituted poly(arylenebuta-1,3-diynylene) **1** and poly(arylene-ethynylene) type polymers **4** could both be produced from the appropriate arylendiyne and that they could be utilised in a variety of ways (Scheme 2).

Scheme 2 outlines some potential polymers derived from diyne precursors **3**. Not only should **3** yield **1** and then **2**, but also **4** by cross-coupling reactions which would allow for the incorporation, in a controlled fashion, of a variety of aryl groups. Hydrogenation of **4** would yield poly(phenylene-vinylene)s³⁹ **5**, whilst reaction of **4** with 1,3-dipolar compounds⁴⁰ would yield a set of heteroaromatic polymers **6** of a quite different constitution from **2**. Reaction of **3** with metal halides should yield polymers **7** incorporating the metal.⁴¹

A conceptually similar approach to **2** which involved the cyclisation of poly(arylene-1,4-diketones) using ammonium acetate and Lawesson's reagent has been described.⁴²

The nearest analogy⁴³ for the conversion of **3** to **1** to **2** involves the reactions of a mixed 'polyethynylbenzene' with H₂S and anilines. The product poly(thienylene-phenylene) were completely insoluble, possibly due to extensive cross linking.

The copper catalysed reactions with anilines were extremely sensitive to oxidants, the presence of which rapidly gave Aniline Black. The product *N*-arylpyrrolylene-phenylene polymers however were soluble but were determined by analysis to be high

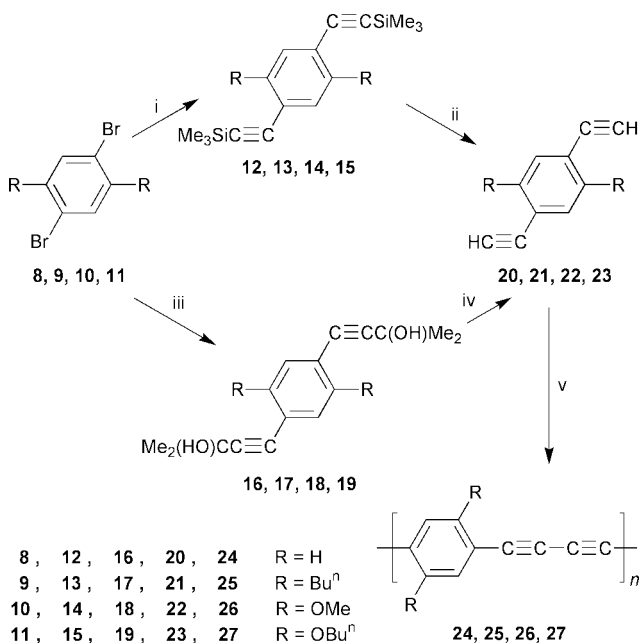


Scheme 2

in nitrogen as a result of 1,3-additions. The polymer from 4-methylaniline had a molecular weight of 86000.

2. Preparation of substituted 1,4-diethynylbenzene monomers

Two routes to give the required 1,4-diethynylbenzenes are shown in Scheme 3. The substituents were chosen based on our



Scheme 3 Reagents and conditions: (i) Pd(PPh₃)₂Cl₂ (cat.), CuI (cat.), HC≡CSiMe₃, **28**, piperidine, 70 °C, 30 h; (ii) K₂CO₃, MeOH, 20 °C; (iii) Pd(PPh₃)₂Cl₂ (cat.), CuI (cat.), HC≡CC(OH)Me₂, **29**, Pr₂NH, 75 °C, 24 h; (iv) NaH, toluene, reflux, 18 h; (v) CuCl, TMEDA, O₂, pyridine, 30 °C, ultrasound.

experience that two *n*-butyl or *n*-butyloxy groups/benzene unit greatly enhanced the solubility of oligomers **2**.¹² As compared with products with R = H the substitution of two 1,4-related *n*-butyl groups should not lead to great perturbations in the electronics of the polymers, but when R = OMe or R = OBUⁿ then interesting electronic as well as solubility effects were expected.

1,4-Dibromobenzene **8** is commercially available and **9**, **10** and **11** were prepared by our previous method.¹² For **8** and **10** the process^{44,45} leading to **12** and **14** and then to **20** and **22** proceeded in acceptable overall yields of 77 and 62% respectively. However when two equivalents of **28** (see Scheme 3) were

reacted with **9** then **13** was obtained in 7% yield only. A large amount of mono-coupled product was isolated together with some starting material. As **28** is expensive it was not desirable to force the reactions by using it in large excess therefore the much cheaper reagent **29** (see Scheme 3) was substituted for **28** for the coupling reactions.^{35–37,46,47}

Reaction of 4.8 equivalents of **29** with **9** gave **17** in 73% yield and deprotection to **21** with sodium hydride^{46,47} proceeded in 51% yield. A similar procedure led from **11** to **19** in 88% yield and from **19** to **23** in 64% yield. Thus the required diethynylbenzenes, **20**, **21**, **22** and **23** were readily available in good quantities and it was unnecessary to make **15**, **16** and **18**.

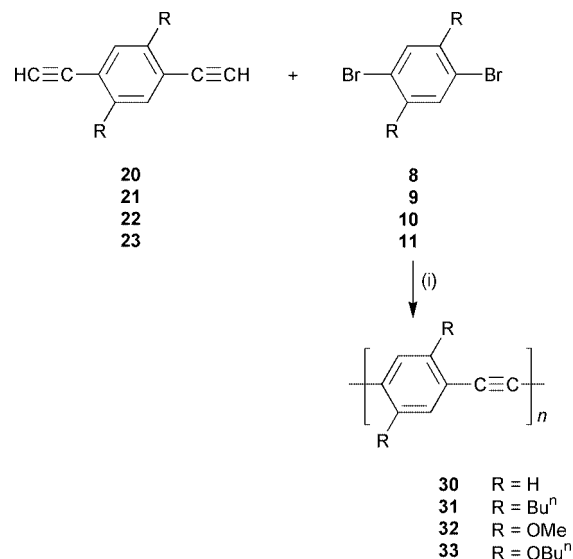
3. Oxidative polymerisations of diynes 20–23

The conditions introduced by Hay^{30–32} were tested on phenylethyne and gave 1,4-diphenylbuta-1,3-diyne in 85% yield. Using the same conditions diyne **20** gave a powder which was finely ground and suspended in methanol–1 M HCl aq. The mixture was sonicated for 5 h so as to remove residual CuCl, pyridine and low molecular weight oligomers, and the remaining solid was collected and dried. All polymeric products were treated in this way. Polymer **24** was obtained as a pale yellow solid which was completely insoluble in petroleum ether, dichloromethane, chloroform, THF and methanol at 50 °C. Polymer **25** was obtained as a bright yellow solid which became black but did not melt below 360 °C. The polymer had a limited solubility in organic solvents, *e.g.* 10 mg dissolved in 30 ml of THF at 50 °C, and was four times more soluble in hot nitrobenzene or anisole. The dimethoxypolymer **26** was obtained as an orange solid with similar solubility to **25** in THF. It did not melt up to 270 °C. Polymer **27** was a yellow–orange solid which also showed limited solubility in organic solvents, *e.g.* 10 mg dissolved in 50 ml THF, 18 ml PhNO₂ or 15 ml of hot anisole.

For all the above polymers unsatisfactory elemental analyses were obtained which may partly be explained by the presence of low molecular weight oligomers giving rise to lower C:H ratios, in a fashion similar to that recorded recently for binaphthylene-ethynylene polymers.⁴⁸

4. Polymerisations by cross-coupling reactions

Scheme 2 outlined a possible synthesis of polymers **4** by cross coupling reactions of **3** with dibromoarenes. We decided to test this, but keeping Ar¹ = Ar² (Scheme 2) as shown in Scheme 4. The same coupling conditions were used as for the preparation of the starting diynes.⁴¹



Scheme 4 Reagents and conditions: (i) Pd(PPh₃)₂Cl₂ (3–4 mol%), CuI (3–4 mol%), Pr₂NH, 70 °C.

The unsubstituted polymer **30** was obtained as a light yellow–brown solid which was completely insoluble in a wide range of organic solvents and did not melt up to 360 °C. Polymer **31** was obtained as a dark red–brown solid which was sufficiently soluble in chloroform (10 mg ml⁻¹) as to allow a solution ¹H NMR spectrum to be obtained. Polymer **31** did not melt up to 360 °C. The dimethoxy polymer **32** was obtained as a pale yellow solid which was slightly soluble in chloroform (10 mg 30 ml⁻¹) and also did not melt up to 360 °C. Polymer **33** came out as a dark reddish-brown solid which was Soxhlet-extracted with toluene for 40 h, on which *ca.* 50% by weight was toluene soluble.

All of polymers **30–33** were treated in the same way as polymers **24–27** in an effort to get rid of inorganic and organic impurities. However elemental analysis in each case deviated greatly from that expected. The greatest cause of impurity is Pr₂NH·HCl which was not completely removed even after sonication for 5 h in an aqueous medium. Thus **32** gave 0.4% nitrogen even after repeated washings with organic solvents, water and methanol. Similar problems of purification have been experienced by others who employed similar polymerisation methods. Thus Corriu *et al.*²⁸ removed Et₂NH·HCl from silicon containing polymers by repeated precipitation from THF–pentane. Marvel and Trumbo³⁶ removed the salt from their acetylenic polymers by repeated washing with 10% HCl, water and methanol followed by repeated precipitation from chloroform–methanol. Bochmann and Kelly³⁸ found as much as 6.7% of residual bromine. The very limited solubilities of our polymers makes purification by the dissolution–precipitation method impractical and purification remains a major problem as with other arylene-ethynylene polymers.⁴⁸ Possibly the use of longer alkyl chains on the benzene rings would enhance solubility and this could be the most promising approach.

5. Molecular weight analyses of polymers 24–27 and 30–33

Molecular weight analyses were carried out by gel permeation chromatography using a polystyrene standard, a method that may overestimate the molecular weight of conjugated polymers by a factor between 1 and 2.^{49,50} For polymers **24** and **30**, total insolubility precluded molecular weight determination. The limited solubility of **26** and **27** meant that only some low molecular weight oligomers were observed. Polymer **32** was sufficiently soluble so that oligomers with *M_w* of 10000 were observed in the soluble fraction. The same was true of **33** which gave *M_w* 10380 and *M_n* 3207 for the soluble fraction. Polymer **25** was somewhat more soluble and *M_w* 46000 and *M_n* 11539 were obtained for the soluble fraction.

In general for molecular weight determinations we have used a 2% w/v solution^{12,51} but we were forced in these cases to use significantly lower concentrations. Even then only the lower molecular weight ‘polymers’ were observed and the results obtained are not a true reflection of the molecular weight of the bulk polymer. However, even the soluble fractions showed peaks ranging from a few thousand up to several hundred thousand.⁵¹ The results show that polymers can be obtained that are of much higher molecular weight than those made by the cross coupling reactions we previously employed. This is as true of the ethynyl cross-coupled polymers **30–33** as of polymers **24–27** obtained by the Hay–Glaser oxidation procedure.

6. Electrical conductivity measurements

The electrical conductivity of both the undoped polymers and the polymers doped with ferric chloride (see Experimental section) was examined and gave the results shown in Table 1.

All the undoped polymers have conductivities, as expected, in the insulator range. Doping has far less effect on the conductivities of these polymers than on polymers **2**.¹² Polymer **24** has been previously prepared^{30,52} and solid state ¹³C NMR suggested that it was defect free and of high molecular weight.

Table 1 Electrical conductivities of polymers **24–27** and **30–33**

| Polymer | Conductivity S/cm ⁻¹ | |
|-----------|---------------------------------|------------------------------|
| | Undoped | Doped with FeCl ₃ |
| 24 | 3.434 × 10 ⁻¹² | 7.326 × 10 ⁻⁹ |
| 25 | 1.330 × 10 ⁻¹¹ | ^a |
| 26 | 5.570 × 10 ⁻¹² | 6.044 × 10 ⁻¹¹ |
| 27 | 2.236 × 10 ⁻¹² | 4.463 × 10 ⁻⁸ |
| 30 | 1.654 × 10 ⁻¹¹ | 2.399 × 10 ⁻¹⁰ |
| 31 | ^a | 2.037 × 10 ⁻⁸ |
| 32 | 1.889 × 10 ⁻¹² | 5.701 × 10 ⁻¹⁰ |
| 33 | 4.112 × 10 ⁻¹¹ | 3.061 × 10 ⁻⁸ |

^a Could not be pressed into a coherent disc.

Iodine doping was reported to increase the conductivity three-fold⁵² as compared with our increase using ferric chloride doping of 2.13 × 10³. The range of increase in conductivity of our diynyl polymers was from 2.0 × 10⁴ for **27** to 10.9 for polymer **26**, the effect of the methoxy substituents being very marked. The increases in the phenylenevinylene polymers **30**, **32**, **33** ranged from 14 to 1.34 × 10³. In both sets the changes were greatest with butyloxy substituents.

Conclusions

The approach adopted has resulted in high molecular weight polymers which however are very difficult to purify. Ongoing work concerns the production of polymers **1** and **4** with more lipophilic substituents, such as R = *n*-hexyl, *n*-octyl, *O-n*-hex, *O-n*-oct, in order to enhance the solubility of the polymers and thus greatly assist their purification and characterisation.

Experimental

General conditions

Trimethylsilylethyne, 2-methylbut-3-yn-2-ol, (Ph₃P)₂PdCl₂, CuI, CuCl, K₂CO₃, NaOH and reagent grade oxygen were commercially available and were used as bought. Sodium hydride (80% dispersion) was stirred with hexane and the hexane removed by a double ended needle. This was repeated at least three times and then the hexane was removed under vacuum. Phenylethyne and piperidine were refluxed over and distilled from CaH₂. Pyridine, TMEDA and diisopropylamine were refluxed over NaOH followed by distillation. Diethyl ether was passed through activated alumina then refluxed over and distilled from CaH₂. THF was passed through activated alumina then refluxed over and distilled from CaH₂. Toluene was shaken with aliquots of ice-cooled conc. H₂SO₄, H₂O, 10% aqueous K₂CO₃, H₂O then dried over CaCl₂ and distilled. Ferric chloride was used from a freshly purchased bottle taking care only to use lustrous, dark green needles.

All procedures, including polymer doping, that involved air sensitive reagents were performed in oven dried glassware that was assembled whilst hot and cooled in a slow stream of dry nitrogen. Transfer of air sensitive chemicals was achieved by using double ended needles under nitrogen or argon pressure or by graduated syringes. Doped polymers were stored over P₂O₅ in a vacuum desiccator. Chromatographic purifications were performed on either silica gel (230–400 mesh) or alumina under medium pressure using mixtures of pentane and chloroform.

Melting points were recorded on a Gallenkamp hot stage apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a WM 250 Bruker instrument at 250.1 and 62.9 MHz respectively. DEPT/135 spectra were also obtained on this instrument. NMR spectra were recorded in CDCl₃ unless otherwise stated and are reported relative to tetramethylsilane (δ = 0). *J* values are quoted in Hz. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrometer

and a UNICAM SP 1050 spectrometer as KBr discs unless otherwise stated. UV–visible spectra were recorded on a Phillips PV 8720 UV–vis scanning spectrophotometer with absorption maxima reported in nm along with ($\log_{10} \epsilon$). Mass spectra were obtained using a VG MASSLAB 12–250 quadrupole instrument using alternating chemical/electron impact ionisation (ACE) conditions. Accurate masses were recorded on a ZAB-E VG analytical reverse geometry magnetic instrument. Elemental analyses were provided by the Microanalytical Service at the University of Wales Cardiff. Molecular weight determinations were carried out at the RARDE (MoD) establishment, Waltham Abbey using a Waters GPC system equipped with Waters Expert Version 4.0 analytical software, and are in polystyrene equivalents. The ultrasonic probe used was a 100 W Ultrasonic Amplifier, type L665. Electrical conductivities were determined by converting the dried powders to discs of 1 cm diameter and 0.5 mm thickness. Slabs of these discs, of known dimensions were cut and the ends coated with colloidal silver. Two platinum wires were attached to the silver and to a 10 point plug. The resistance was measured using a Keithley 602 programmable electrometer.

Preparation of arylidyne monomers

1,4-Bis(trimethylsilylethynyl)benzene, 12. Trimethylsilylethyne **28** (7.7 g, 38.6 mmol) was added by syringe to a 500 ml round-bottomed flask containing a well stirred mixture of 1,4-dibromobenzene (9.1 g, 38.6 mmol), Pd(PPh₃)₂Cl₂ (0.3 g, 0.43 mmol, 1.1 mol%), CuI (0.14 g, 0.74 mmol) and diisopropylamine (150 ml). The resultant mixture was stirred at 70 °C for 3.5 h. The solvent was removed and the grey–black residue was placed on alumina (100 g) and eluted with petroleum spirit (40–60 °C). Compound **12** (10 g, 96%) was obtained as white crystals, mp 122 °C (lit.⁵² 122 °C). δ_{H} 7.39 (4H, s), 0.24 (18H, s). δ_{C} 104.5, 96.2 (C≡CH), 131 (d, (Ar)CH), 123.1 ((Ar)C≡C), –0.21 (Si-CH₃). λ_{max} (CHCl₃) 279.6 (3.59), 287.8 (3.44), 294.1 (3.67). $\nu_{\text{max}}/\text{cm}^{-1}$ 2150 (C≡C stretch). m/z 270, 255, 240, 225, 210, 195, 180. Found, M⁺, 270.1260. C₁₆H₂₂Si₂ requires 270.1259.

2,5-Bis(trimethylsilylethynyl)-1,4-dimethoxybenzene, 14. A mixture of 1,4-dimethoxy-2,5-dibromobenzene¹² (15 g, 50.7 mmol), Pd(PPh₃)₂Cl₂ (0.38 g, 0.54 mmol, 1.1 mol%), CuI (0.1 g, 0.53 mmol) and piperidine (150 ml) was well stirred in a 500 ml round-bottomed flask. Trimethylsilylethyne **28** (10 g, 102 mmol) was added by syringe and the reaction mixture stirred at 70 °C for 6 h. The solvent was evaporated and **14** (12 g, 71%) was obtained as pale yellow crystals, mp 162–163 °C, by elution with light petroleum from alumina. δ_{H} 6.29 (2H, s, Ar-H), 3.83 (6H, s, OCH₃), 0.27 (18H, s, Si(CH₃)₃). δ_{C} 0.12 (Si-CH₃), 56.55 (OCH₃), 100.5, 101.0 (C≡C), 113.7 ((Ar)C≡C), 116.4 (Ar-CH), 154.35 (Ar, C-OCH₃). λ_{max} (CHCl₃) 241.3 (3.19), 271.1 (3.40), 287.2 (3.67), 355.2 (3.17). $\nu_{\text{max}}/\text{cm}^{-1}$ 2140 (C≡C stretch). m/z 330, 315, 300, 285, 270, 255, 240, 225. Found, C 65.46; H, 7.87%; M⁺, 330.1471. C₁₈H₂₆O₂Si₂ requires C, 65.5; H, 7.9%; M⁺, 330.14698.

1,4-Bis(trimethylsilylethynyl)-2,5-di-*n*-butylbenzene, 13. Piperidine (50 ml), 1,4-dibromo-2,5-di-*n*-butylbenzene **9** (3.1 g, 8.1 mmol), Pd(PPh₃)₂Cl₂ (0.167 g, 0.24 mmol, 2.9 mol%) and CuI (0.056 g, 0.29 mmol) were stirred in a 250 ml round-bottomed flask. Trimethylsilylethyne **28** (1.8 g, 18.4 mmol) was added and the reaction mixture was stirred at 70 °C for 30 h. The solvent was removed and the residue was chromatographed twice through alumina (2 × 200 g) using light petroleum (40–60 °C) as eluent. Compound **13** was obtained as light brown crystals which on crystallisation from ethanol–water gave **13** (0.19 g, 7%) as cream coloured needles, mp 53–55 °C. δ_{H} 7.24 (2H, s, Ar-H), 2.69 (4H, t, Ar-CH₂-), 1.58 (4H, m, (Ar)CH₂CH₂-), 1.37 (4H, m, CH₂-CH₃), 0.93 (6H, t, CH₃-CH₂-),

0.25 (18H, s, Si-CH₃). δ_{C} 0.44 (Si-CH₃), 14.41 (CH₃CH₂), 23.11 (CH₂CH₃), 33.17 (Ar-CH₂CH₂-), 34.25 (Ar-CH₂-CH₂), 99.39 (C≡C-SiMe₃), 104.48 (Ar-C≡C-), 123.1 (C-1), 132.98 (C-3), 143.09 (C-2). m/z 382, 367, 351, 339, 310, 295, 280. Found, C, 75.25; H, 9.99%; M⁺, 382.2512. C₂₄H₃₈Si₂ requires C, 75.4; H, 9.9%; M⁺, 382.2510.

1,4-Bis(3-hydroxy-3-methylbut-1-ynyl)-2,5-di-*n*-butylbenzene, 17. A mixture of 1,4-dibromo-2,5-di-*n*-butylbenzene **9** (9.0 g, 25.8 mmol), Pd(PPh₃)₂Cl₂ (0.51 g, 0.73 mmol, 2.8 mol%), CuI (0.15 g, 0.79 mmol), and 2-methylbut-3-yn-2-ol, **29** in Pr₃NH (200 ml) was stirred at 75 °C for 24 h. Removal of the solvent was followed by chromatography on silica gel (500 g) using petroleum ether (40–60 °C) and chloroform mixtures. The product (6.7 g, 73%) was obtained as pale yellow needles, mp 130–132 °C. δ_{H} 7.19 (2H, s, H-3), 2.65 (4H, t, Ar-CH₂-), 2.35 (2H, s, OH), 1.62 (12H, s, CH₃-C(OH)), 1.54 (4H, m, Ar-CH₂-CH₂-), 1.36 (4H, m, CH₂-CH₃), 0.93 (6H, t, CH₂-CH₃). δ_{C} 142.21 (C-2), 132.44 (C-3), 122.15 (C-1), 98.35 (Ar-C≡C), 81.1 (Ar C≡C-), 65.87 (CMe₂), 33.81 (ArCH₂), 32.82 (Ar CH₂CH₂-), 22.7 (CH₂CH₃), 14.11 (CH₃CH₂-). λ_{max} 272 (4.45), 280.5 (4.48). m/z , 354, 339, 297. Found, C, 81.42; H, 9.76%; M⁺, 354.2559. C₂₄H₃₄O₂ requires C, 81.4; H, 9.6%; M⁺, 354.2557.

1,4-Bis(3-hydroxy-3-methylbut-1-ynyl)-2,5-di-*n*-butoxybenzene, 19. A 500 ml round-bottomed flask was charged with 1,4-dibromo-2,5-di-*n*-butoxybenzene, **11** (15 g, 39.5 mmol), Pd(PPh₃)₂Cl₂ (0.4 g, 0.37 mmol, 1.4 mol%), CuI (0.19 g, 1 mmol), **29** (15 g, 179 mmol, 4.5 equiv.) and Pr₃NH (250 ml). The reaction mixture was stirred at 70 °C for 18 h, the solvent was evaporated and the residue was purified on silica (500 g) using CHCl₃ as eluent. Brown needles (15 g) were obtained and on crystallisation from acetone–water, and the product **19** (13.2 g, 88%) was isolated as fine white needles, mp 139–141 °C. δ_{H} 6.82 (2H, s, H-3), 3.92 (4H, t, OCH₂), 2.90 (2H, s, HO-), 1.76 (4H, m, OCH₂CH₂-), 1.61 (12H, s, C(OH)-CH₃), 1.51 (4H, m, CH₂CH₃), 0.97 (6H, t, CH₃CH₂-). δ_{C} 153.56 (C-2), 117.13 (C-3), 113.48 (C-1), 99.28 (C-4'), 78.37 (C-3'), 31.4 (O-CH₂CH₂ and C-2'), 19.20 (CH₂CH₃), 13.85 (CH₃-CH₂-). λ_{max} 269.9 (4.73), 278 (4.87), 338 (4.11). m/z 386, 328. Found, C, 74.78; H, 9.08%; M⁺, 386.2457. C₂₄H₃₄O₄ requires C, 74.6; H, 8.8%; M⁺, 386.2455.

1,4-Diethynylbenzene, 20.⁵² Potassium carbonate (0.25 g, 1.85 mmol) was added to a 250 ml round-bottomed flask charged with **12** (0.5 g, 1.85 mmol) and methanol (100 ml). The mixture was stirred at room temperature for 16 h during which time the K₂CO₃ dissolved. Water (200 ml) was added and the precipitate was filtered and dried under reduced pressure at room temperature. Product **20** was obtained as white crystals mp 95–96 °C (lit.⁴⁴ 95–96 °C). δ_{H} 3.17 (2H, s, H-C≡C), 7.44 (4H, s, Ar-H). δ_{C} 132.18 (C-2), 127.77 (C-1), 83.22 (Ar C≡C), 79.21 (C≡CH). λ_{max} (CHCl₃) 262.3 (4.39), 275 (4.45). $\nu_{\text{max}}/\text{cm}^{-1}$ 3270 (C≡C-H).

2,5-Diethynyl-1,4-dimethoxybenzene, 22.⁵³ Compound **14** (4.5 g, 13.6 mmol) dissolved in MeOH (150 ml) was stirred with K₂CO₃, (4 g, 29 mmol) for 12 h at room temperature. Water (200 ml) was added and the product (2.2 g, 87%) was collected as white crystals, mp 163–166 °C (lit.⁵³ 153–154 °C). δ_{H} 6.97 (2H, s, C-1), 3.85 (6H, s, OCH₃), 3.39 (2H, s, C≡C-H). δ_{C} 154.47 (C-1), 116.27 (C-2), 112.75 (C-3), 82.12 (ArC≡CH), 79.7 (C≡CH). λ_{max} 243.1 (3.89), 263.7 (4.18), 272.5 (4.22), 347.3 (3.95). $\nu_{\text{max}}/\text{cm}^{-1}$ 3260 (C≡C-H stretch).

1,4-Diethynyl-2,5-di-*n*-butylbenzene, 21. Sodium hydride (2.5 g, 104 mmol) was added to a solution of **17** (10.5 g, 29.6 mmol) in toluene (150 ml). The mixture was heated under reflux for 16 h then cooled and the supernatant liquid was decanted from the solid in the bottom of the flask. The solvent was evaporated leaving a viscous blood-red liquid which was placed on silica (250 g) and eluted with petroleum spirit (30–40 °C). Product **21**

(3.5 g, 50%) was obtained as a pale yellow liquid which turned to orange even on standing in the dark under nitrogen. The material solidified to a blood-red gel-like substance when reduced pressure distillation was attempted. δ_{H} 7.27 (2H, s, H-3), 3.2 (2H, s, C≡C-H), 2.7 (4H, t, Ar-CH₂CH₂), 1.58 (4H, m, Ar-CH₂CH₂), 1.34 (4H, m, CH₂CH₃), 0.9 (6H, t, CH₂CH₃). δ_{C} 142.62 (C(Ar)-Bu), 133.04 (C-3), 122.16 (Ar(C)-C≡CH), 82.36 (Ar-C≡CH), 81.66 (Ar-C≡CH), 33.66 (Ar-CH₂), 32.82 (Ar-CH₂CH₂-), 22.63 (CH₂CH₃), 14.0 (CH₂CH₃). Found, C, 89.65; H, 9.89%. C₁₈H₂₂ requires C, 90.8; H, 9.2%.

1,4-Di-*n*-butoxy-2,5-diethynylbenzene, 23. A 250 ml round-bottomed flask was charged with a solution of **19** (18 g, 46.6 mmol) in toluene (175 ml). Sodium hydride (5.5 g, 229 mmol) was added and the mixture heated under reflux for 12 h. The liquid was decanted from the solid residue, evaporated and the red residue chromatographed on silica (500 g) using as eluent a mixture of light petroleum and chloroform (1:1). **Product 23** was obtained as pale green needles, mp 102–104 °C (8 g, 64%). δ_{H} 6.96 (H-3), 3.97 (4H, t, CH₂-O), 3.34 (2H, s, C≡CH), 1.77 (4H, m, OCH₂CH₂), 1.49 (4H, m, CH₂CH₃), 0.95 (6H, t, CH₃).

Preparation of aryldiyne polymers

Poly(1,4-phenylenebuta-1,3-diyne), 24. Oxygen was bubbled into a sonicated 250 ml round-bottomed flask containing CuCl (0.2 g, 2 mmol), TMEDA (0.5 g, 4.3 mmol) and pyridine (50 ml) at 32 °C. A solution of 1,4-diethynylbenzene, **20** (0.7 g, 5.6 mmol) in pyridine (30 ml), also at 32 °C, was added rapidly and the mixture left at 32 °C for 16 h. Evaporation of the solvent gave a green solid which was suspended in a mixture of methanol (50 ml) and aqueous 1 M HCl (50 ml) and sonicated for 3 h. The very fine yellow powder that resulted was filtered, washed with water and dried at 40 °C/0.1 mmHg for 2 h and then for 16 h at room temperature. This process gave **24** (0.6 g, 86%). λ_{max} 331.9, 341.5, 355.3. Found, C, 91.57; H, 4.05%. (C₁₀H₄)_n requires C, 96.8; H, 3.2%.

Poly(2,5-di-*n*-butyl-1,4-phenylene)buta-1,3-diyne, 25. A solution of **21** (4.9 g, 18.1 mmol) in pyridine (50 ml) was added to a sonicated 3-necked 250 ml round-bottomed flask charged with CuCl (0.7 g, 7.1 mmol), TMEDA (0.8 g, 6.9 mmol) and pyridine (150 ml) at 52 °C through which oxygen was bubbled. During the addition the temperature rose to 65 °C. The reaction was continued at 55 °C for 19 h, solvent was evaporated and the product obtained as for **24**. The product was reprecipitated from chloroform–acetone and dried at room temperature under reduced pressure to give product **25** (2.8 g, 82%) as a yellow powder. δ_{H} 7.35 (2H, br s, Ar-H), 2.76 (4H, br t, Ar-CH₂), 1.6 (4H, br m, Ar-CH₂CH₂), 0.97 (6H, t, CH₃). λ_{max} 247.6, 280.8, 369.0, 395.7. Found, C, 88.77; H, 8.76%. (C₁₈H₂₀)_n requires C, 91.5; H, 8.5%.

Poly(2,5-dimethoxy-1,4-phenylene)buta-1,3-diyne, 26. The same procedure as for **25** was used, the quantities being **22** (2.4 g, 12.9 mmol), CuCl (0.3 g, 3 mmol), TMEDA (0.5 g, 4.3 mmol) and pyridine (160 ml). The reaction temperature was 45 °C and the reaction time was 14.5 h. Work-up as before gave **26** (2.8 g) as an orange solid which had very low solubility in most organic solvents. λ_{max} (CHCl₃) 409. Found, C, 74.0; H, 4.7%. (C₁₂H₈O₂)_n requires C, 78.2; H, 4.3%.

Poly(2,5-di-*n*-butyloxy-1,4-phenylene)buta-1,3-diyne, 27. The same procedure as for **24** and **25** was followed. Monomer **23** (4.9 g, 18.1 mmol) in pyridine was added to a mixture of CuCl (0.54 g, 5.5 mmol), TMEDA (1.05 g, 9 mmol) and pyridine (120 ml) at 53 °C. The temperature rose to 83 °C during the 13 h reaction time. Solvent was removed and the usual work-up gave **product 27** (2.2 g, 45%) as an orange solid.

λ_{max} (CHCl₃) 243.0, 349.6, 428.0. Found, C, 80.7; H, 7.67%. (C₁₈H₂₀O₂)_n requires C, 80.6; H, 7.5%.

Preparation of arylylene-ethynylene polymers

Poly(1,4-phenyleneethynylene), 30. A solution of 1,4-diethynylbenzene **20** (2.9 g, 23 mmol), 1,4-dibromobenzene **8** (5.4 g, 22.8 mmol), Pd(PPh₃)₂Cl₂ (0.5 g, 0.71 mmol, 3.1 mol%), CuI (0.13 g, 0.68 mmol) and Pr₂NH (100 ml) was stirred at 75 °C for 40 min after which time the precipitate was so thick that stirring was not possible. The solvent was removed to give a light green residue which was finely ground and suspended in a mixture of methanol (200 ml) and aqueous HCl (3 M, 100 ml). The suspension was subjected to ultra-sound for 2 h, filtered and the residue washed with methanol and then ether. **Product 30** (4.5 g, 98%) was obtained as a brown solid after being dried in a desiccator at room temperature. λ_{max} (CHCl₃) 240, 330.

Poly[(2,5-di-*n*-butyl-1,4-phenylene)ethynylene], 31. The same method as for **30** was used, the quantities being 1,4-diethynyl-2,5-di-*n*-butylbenzene (1.85 g, 7.8 mmol), 1,4-dibromo-2,5-diethynylbenzene, **9** (2.7 g, 7.8 mmol), Pd(PPh₃)₂Cl₂ (0.18 g, 0.26 mmol, 3.3 mol%), CuI (0.1 g, 0.53 mmol, 6.4 mol%) and Pr₂NH (100 ml). The reaction on cooling gave a solid precipitate, and on addition of methanol, more precipitate was obtained and worked up as for **30**. The green powder that resulted was dissolved in chloroform, washed with water, dried over CaCO₃, filtered and the solvent removed to give a dark reddish brown solid (1.5 g). δ_{H} 7.37 (2H, br m, Ar-H), 2.7 (4H, br m, Ar-CH₂), 1.64 (4H, br m, Ar-CH₂CH₂), 1.44 (4H, br m, CH₂CH₃), 0.98 (6H, br m, CH₃). λ_{max} (CHCl₃), 244.0, 387.0. Found, C, 83.3; H, 8.9%. (C₁₆H₂₀)_n requires C, 90.6; H, 9.4%.

Poly[(2,5-dimethoxy-1,4-phenylene)ethynylene], 32. A mixture of **22** (2.2 g, 11.8 mmol), **10** (3.5 g, 11.8 mmol), Pd(PPh₃)₂Cl₂ (0.23 g, 0.33 mmol, 2.8 mol%), CuI (0.065 g, 0.34 mmol) and Pr₂NH (125 ml) was stirred at 70 °C for 16 h. The usual work-up as for **30** gave **product 32** (4.4 g) as a pale yellow, insoluble polymer. λ_{max} (CHCl₃) 303, 408.

Poly[(2,5-di-*n*-butyloxy-1,4-phenylene)ethynylene], 33. Following the general procedure for **30** a mixture of **23** (2.0 g, 7.4 mmol), **11** (2.8 g, 7.4 mmol), Pd(PPh₃)₂Cl₂ (0.2 g, 0.28 mmol, 3.9 mol%) and CuI (0.13 g, 0.68 mmol) in Pr₂NH (150 ml) was stirred for 15 h at 75 °C. The usual work-up gave a reddish brown solid which was subjected to 48 h extraction with toluene in a Soxhlet extractor. This gave a soluble fraction (0.8 g) with δ_{H} 7.08 (2H, br s, Ar-H), 4.02 (4H, m, OCH₂), 1.84 (4H, br m, O-CH₂CH₂), 1.63 (4H, br m, CH₂CH₃), 1.0 (6H, m, CH₃). λ_{max} (CHCl₃) 243.0, 436.0. The insoluble fraction (0.9 g) had C, 73.7; H, 7.7%. (C₁₆H₂₀)_n requires C, 78.7; H, 8.2%.

Doping experiments

Insoluble polymers. A saturated solution of FeCl₃ in nitromethane was prepared by stirring a large excess of FeCl₃ with nitromethane for 3 h. The solution was decanted by cannula under nitrogen pressure. The polymer samples (0.2 g) were thoroughly ground up and stirred for 12 h at room temperature with the FeCl₃ solution then rapidly pressed into discs using a standard IR press. The discs were kept in an active desiccator over P₂O₅ under reduced pressure prior to resistivity measurements.

Soluble polymers. Polymer (0.2 g) was dissolved in chloroform and stirred with solid FeCl₃ (0.4 g) for 15 h at room temperature. The solvent was removed and evaporated and the residues washed thoroughly with ether, dried and pressed into discs.

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