

Synthesis of novel poly(dithienylpyridines)[†]

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This paper describes the chemical and electrochemical synthesis of novel copolymers of thiophene and pyridine. Di-iodination of 3-hydroxypyridine **12** followed by *O*-substitution gave a series of ethers **14b–d** and esters/carbamates **15a–d** which were reacted with the stannylated bithiophene derivative **17** in a Stille cross-coupling reaction yielding poly (**1b–d**) and poly (**2a–d**) respectively. These chemical polymerisation reactions generally resulted in highly insoluble materials which were difficult to characterise. Ethers **14b–d** and esters/carbamates **15a–d** gave *O*-substituted 3-hydroxy-2,6-di(2-thienyl)pyridines **1b–d** and **2a–d** respectively in Stille cross-coupling reactions with the stannylated thiophene **16**. Ethers **1b–d** underwent electrochemical polymerisation allowing the synthesis of *O*-alkylated polymers, poly (**1b–d**), with electrochemical band-gaps of 1.4 to 1.6 eV. In contrast, the esters/carbamates **2a–d** could not be electropolymerised.

Introduction

Recently, there has been considerable interest in the synthesis of organic polymers which might act as conductors in either the doped or un-doped state and would therefore have the potential to function as organic metals in electronic devices. One of the main advantages of organic polymers as organic metals over inorganic materials is their potential for processing. Polythiophenes and substituted polythiophenes^{1–3} have been extensively studied as conducting polymers and their synthesis and properties continue to attract considerable interest. Although polythiophene has the disadvantage of being insoluble which limits its potential for processing, substituted polythiophenes possessing aliphatic or polar substituents frequently have improved solubility characteristics.

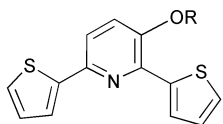
One fundamental challenge in polythiophene chemistry has been to prepare low band-gap materials. This is often achieved by introducing pendant substituents onto the polymer backbone in order to increase the energy of the highest occupied molecular orbital (HOMO) or reduce the energy of the lowest unoccupied molecular orbital (LUMO). Band-gap energies can be readily determined from the low energy absorption edge of their electronic spectra or by cyclic voltammetry. Band-gaps in polythiophenes are typically about 2 eV although some polymers have been reported with significantly lower band-gaps, for example the band-gap in regioregular polyalkylthiophenes was determined as 1.7 eV.⁴ We have been interested in preparing a series of polythiophene analogues [poly (**1**)–(**4**)] which possess an electron-rich pyridine ring as part of the polymer backbone. In particular, we anticipated that the band-gaps in poly (**3**) might be significantly lower than the band-gaps in poly (**1**) and (**2**) for the reasons which are now outlined. The pyridinium-3-olate **5** is a mesomeric betaine^{5–7} in which the HOMO is distributed over the carbon atoms at the 2,4 and 6-positions and the exocyclic oxygen atom as shown in formula **6**. The HOMO of mesomeric betaine **5** is therefore topologically and energetically similar to a non-bonding molecular orbital

(NBMO). In contrast, the covalent isomer **7** of the mesomeric betaine **5** is associated with an energetically lower HOMO. Thus, the NBMO–LUMO energy difference in mesomeric betaine **5** is significantly smaller than the HOMO–LUMO energy difference in 3-methoxypyridine **7**. The relatively low energy NBMO–LUMO is a general property of heterocyclic mesomeric betaines derived from odd-alternant hydrocarbon anions of which compound **5** is just one of many examples.⁶ Since the NBMO coefficients of mesomeric betaine **5** are located at carbon atoms 2,4 and 6 of the pyridine ring, the substitution of two thienyl groups at any of these positions will lead to polymers in which the positive and negative charges can be delocalised through the polymer backbone. We have chosen the 2,6-disubstitution pattern for our studies *i.e.* monomer **3** from which the corresponding poly (**3**) compounds are derived. Pyridine *N*-oxide **8** is also associated with a HOMO which has similar characteristics to a NBMO. Thus, our interest in dithienylpyridine copolymers also includes the polymers poly (**4a,b**) which possess a pyridine *N*-oxide moiety as the electron-rich pyridine component. In view of the novelty of poly (**1**) and (**2**), we were also interested in preparing and studying these materials.

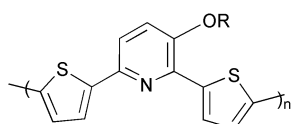
Related work in this area of copolymer chemistry includes Yamamoto and co-workers' studies of thienylpyridine copolymers **9** in which the pyridine unit is substituted at the 2 and 5 positions by 2-thienyl moieties.^{8–11} These copolymers **9** behave as 'charge transfer' materials because of the alternating motif of electron-rich and electron-deficient heterocyclic rings. This work has been extended to include copolymers **10** of thiophene and pyrido[3,4-*b*]pyrazine.^{11,12} Significant differences would be expected between the electronic properties of poly (**3**), (**4**) systems and copolymers **9** because of the different nature of their HOMOs. Higgins and Crayston have prepared polymer **11** by electropolymerisation of 2,6-bis(2-thienyl)pyridine.¹³ Their work did not include pyridines with electron-releasing substituents.

This paper describes our preliminary studies of potential low band-gap polythiophene analogues in which the polymer backbone consists of both thiophene and electron-rich pyridine

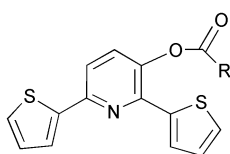
[†]Electronic supplementary information (ESI) available: further experimental details. See <http://www.rsc.org/suppdata/jm/b2/b201229d/>



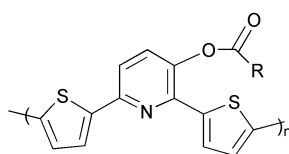
- 1a R = H
 1b R = Me
 1c R = n-hexyl
 1d R = benzyl



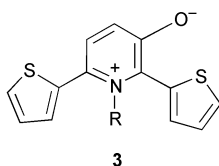
Poly (1a-d)



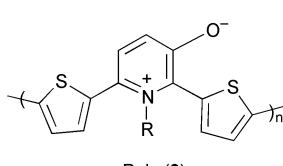
- 2a R = Me
 2b R = n-pentyl
 2c R = phenyl
 2d R = NEt₂



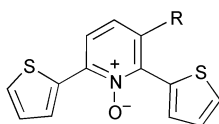
Poly (2a-d)



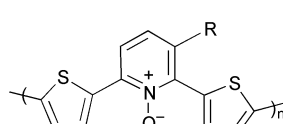
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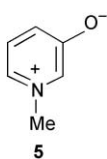
Poly (3)



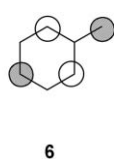
- 4a R = H
 4b R = OMe



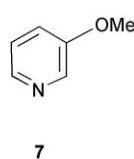
Poly (4a,b)



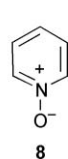
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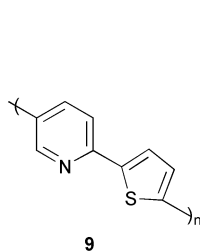


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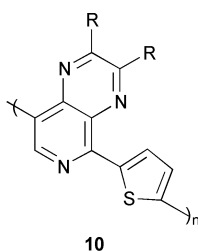


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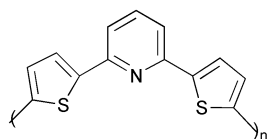
rings. Poly (1–4) have been represented as regioregular polymers for simplicity but the polymers we describe in this paper are probably regio-irregular.



9



10



11

Experimental

General

The following compounds were prepared by literature procedures: **13**,¹⁴ **14b**,¹⁵ **15a**,¹⁵ **17**,¹⁸ **21**,¹⁹ **22**²⁰ and 2-ethynylthiophene.¹⁶ NMR spectra were determined at 270 MHz.

Petroleum ether refers to the fraction bp 40–60 °C. The synthesis of the monomers **1b–1d** used in electropolymerisation reactions and the precursors **14c** and **14d** of these monomers is described below. The synthesis of all other compounds are reported in the electronic supplementary information.†

Synthesis of 2,6-diiodopyridines

2,6-Diiodo-3-hexyloxy pyridine 14c. A mixture of potassium carbonate (3.98 g; 28.8 mmol), hexyl iodide (3.36 g; 15.8 mmol), 2,6-diiodo-3-hydroxypyridine **13** (5.00 g; 14.0 mmol) and dry propanone (40 mL) was heated at reflux for 8 hours. The mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. Dichloromethane (20 mL) was added to the residue and the mixture was then washed with distilled water (3 × 20 mL). The organic layer was dried (MgSO₄), filtered, and evaporated under reduced pressure. The product was then recrystallised from ethanol giving compound **14c** (4.88 g; 79%) as white crystals, mp 52–54 °C. IR (KBr): ν_{\max} 3438, 2927, 2855, 1654, 1551, 1535, 1466, 1417, 1383, 1278, 1227, 1143, 1094, 1072 and 1049 cm⁻¹; ¹H NMR (CDCl₃): δ 7.52 (1H, d, *J* = 8 Hz, Ar*H*), 6.66 (1H, d, *J* = 8 Hz, Ar*H*), 3.99 (2H, t, *J* = 6 Hz, -OCH₂-), 1.84 (2H, m, *J* = 6 Hz, -OCH₂CH₂-), 1.56–1.45 (2H, broad m, -OCH₂CH₂CH₂-), 1.43–1.24 (4H, broad m, -CH₂CH₂CH₃) and 0.91 (3H, t, *J* = 7 Hz, -CH₃) ppm; ¹³C NMR (CDCl₃): δ 155.4, 134.1, 119.7, 111.1, 103.1, 69.7, 31.4, 28.7, 25.6, 22.5 and 14.0 ppm; elemental analysis: C₁₁H₁₅I₂NO requires C, 30.65; H, 3.5; N, 3.25. Found C, 30.6; H, 3.25; N, 3.3%; MS (ES) calculated mass 431.9321, measured mass 431.9321.

2,6-Diiodo-3-benzyloxy pyridine 14d

A mixture of propanone (40 mL), potassium carbonate (8.07 g; 58.0 mmol), benzyl bromide (5.42 g; 32.0 mmol) and 2,6-diiodo-3-hydroxypyridine **13** (10.00 g; 29.0 mmol) was heated at reflux for 8 hours. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. Dichloromethane (20 mL) was added to the residue and the mixture was washed with distilled water (3 × 20 mL). The organic layer was dried (MgSO₄), filtered and evaporated under reduced pressure. The residue was extracted with three portions of hot hexane to remove any remaining benzyl bromide. The crude product was then recrystallised from ethanol giving compound **14d** (5.00 g; 40%) as white crystals, mp 112–114 °C. IR (KBr): ν_{\max} 3414, 1637, 1617, 1544, 1498, 1455, 1411, 1376, 1341, 1278, 1226, 1099, 1056 and 1019 cm⁻¹; ¹H NMR (CDCl₃): δ 7.51 (1H, d, *J* = 8 Hz, Ar*H*), 7.46–7.31 (5H, m, Ar*H*), 6.73 (1H, d, *J* = 9 Hz, Ar*H*) and 5.15 (2H, s, -CH₂-) ppm; ¹³C NMR (CDCl₃): δ 155.2, 135.3, 134.4, 129.0, 128.9, 127.4, 120.9, 111.5, 104.2 and 71.5 ppm; elemental analysis: C₁₂H₉I₂NO requires C, 33.0; H, 2.1; N, 3.2. Found C, 33.0; H, 1.9; N, 3.1%; MS (ES) calculated mass 437.8852, measured mass 437.8859.

Synthesis of 2,6-bis(2-thienyl)pyridines

3-Methoxy-2,6-bis(2-thienyl)pyridine 1b. Under a nitrogen atmosphere a mixture of magnesium (0.34 g; 14.0 mmol), 2-bromothiophene (2.29 g; 14 mmol), a crystal of iodine and dry tetrahydrofuran (10 mL) was stirred and warmed gently until the Grignard reagent had formed. The solution was then cooled to -5 °C and a mixture of 2,6-diiodo-3-methoxy pyridine **14b** (2.00 g; 5.5 mmol), Ni(dppe)Cl₂ (0.054 g; 0.098 mmol) in dry tetrahydrofuran (10 mL) was added dropwise with stirring. The mixture was stirred and slowly warmed to reflux. The mixture was heated at reflux for 20 hours, allowed to cool to room temperature, poured onto ice and extracted with dichloromethane (3 × 30 mL). The organic layers were combined, dried (MgSO₄) and evaporated under reduced pressure. The dark solid was then purified by column

chromatography over silica gel (eluent; ethyl acetate:petroleum ether, 3:7) giving compound **1b** (0.70 g; 46%) as yellow crystals, mp 95–96 °C. IR (KBr): ν_{\max} 3440, 3100, 2938, 1654, 1566, 1465, 1437, 1388, 1334, 1281, 1265, 1202, 1178, 1138, 1082, 1054, 1025 and 1011 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.02 (1H, dd, $J = 1$ and 4 Hz, ArH), 7.47 (1H, dd, $J = 1$ and 4 Hz, ArH), 7.44–7.39 (2H, m, ArH), 7.32 (1H, dd, $J = 1$ and 5 Hz, ArH), 7.19 (1H, d, $J = 9$ Hz, ArH), 7.12 (1H, dd, $J = 4$ and 5 Hz, ArH), 7.06 (1H, dd, $J = 4$ and 5 Hz, ArH) and 3.93 (3H, s, $-\text{OCH}_3$) ppm; ^{13}C NMR (CDCl_3): δ 150.9, 144.9, 144.3, 142.0, 141.4, 128.2, 127.9, 127.8, 127.7, 126.6, 123.3, 119.3, 117.4 and 55.7 ppm; elemental analysis: $\text{C}_{14}\text{H}_{11}\text{NOS}_2$ requires C, 61.5; H, 4.1; N, 5.1. Found C, 61.3; H, 3.85; N, 5.1%; MS (EI) calculated mass 273.0282, measured mass 273.0279.

Stille reactions: general method

Under a nitrogen atmosphere a solution of the appropriate 2,6-diiodopyridine or 2,6-dibromopyridine derivative (1.00 g), 2.2 mol equivalents of 2-(tributylstannyl)thiophene, toluene (40 mL) and 0.11 mol equivalents of tetrakis(triphenylphosphine)palladium(0) was stirred at reflux for 24 hours. The solution was cooled to room temperature and was filtered to remove any precipitated palladium. The mother liquor was evaporated under reduced pressure, dichloromethane (40 mL) was added to the residue and the mixture was washed with 2 M potassium fluoride solution (2×40 mL) and then with distilled water (1×40 mL). The crude product was purified by column chromatography over silica gel (eluent: petroleum ether to remove the tin residues and then ethyl acetate: petroleum ether, 3:7 to elute the product). Using this method the following compounds were prepared.

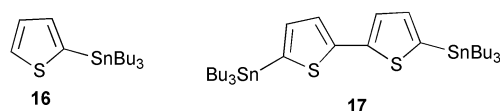
3-Hexyloxy-2,6-bis(2-thienyl)pyridine 1c. The crude product was recrystallised from ethanol giving compound **1c** (0.25 g; 31%) as light yellow crystals, mp 84 °C (with decomposition). IR (KBr): ν_{\max} 3446, 3066, 2916, 2849, 1564, 1460, 1426, 1390, 1337, 1268, 1201, 1135, 1057 and 1022 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.02 (1H, dd, $J = 1$ and 4 Hz, ArH), 7.49 (1H, dd, $J = 1$ and 4 Hz, ArH), 7.45 (1H, d, $J = 8$, ArH), 7.41 (1H, dd, $J = 1$ and 5 Hz, ArH), 7.32 (1H, dd, $J = 1$ and 5 Hz, ArH), 7.22 (1H, d, $J = 8$ Hz, ArH), 7.13 (1H, dd, $J = 4$ and 5 Hz, ArH), 7.08 (1H, dd, $J = 4$ and 5 Hz, ArH), 4.11 (2H, t, $J = 7$ Hz, $-\text{OCH}_2-$), 1.94 (2H, m, $-\text{OCH}_2\text{CH}_2-$), 1.55 (2H, broad m, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.44–1.32 (4H, broad $-\text{CH}_2\text{CH}_2\text{CH}_3$) and 0.92 (3H, t, $J = 6$ Hz, $-\text{CH}_3$) ppm; ^{13}C NMR (CDCl_3): δ 150.2, 144.9, 144.0, 141.9, 141.2, 127.9, 127.8, 127.7, 127.5, 126.4, 123.0, 129.7, 117.2, 68.9, 31.5, 29.1, 25.8, 22.5 and 14.0 ppm; elemental analysis: $\text{C}_{19}\text{H}_{21}\text{NOS}_2$ requires C, 66.4; H, 6.2; N, 4.1. Found C, 66.35; H, 6.2; N, 4.0%. MS (EI) calculated mass 343.1065, measured mass 343.1077.

3-Benzyloxy-2,6-bis(2-thienyl)pyridine 1d. The crude product was recrystallised from ethanol to give compound **1d** (0.15 g; 19%) as white crystals, mp 107–109 °C. IR (KBr): ν_{\max} 3442, 3029, 2883, 1552, 1450, 1377, 1276, 1197, 1141 and 1000 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.01 (1H, dd, $J = 1$ and 4 Hz, ArH), 7.43–7.33 (8H, m, ArH), 7.30 (1H, dd, $J = 1$ and 5 Hz, ArH), 7.16 (1H, d, $J = 9$ Hz, ArH), 7.11–7.02 (2H, m, ArH) and 5.12 (2H, s, $-\text{OCH}_2-$) ppm; ^{13}C NMR (CDCl_3): δ 149.8, 144.9, 144.6, 142.1, 141.6, 128.8, 128.4, 128.4, 128.0, 127.9, 127.8, 127.8, 127.6, 126.7, 123.5, 120.7, 117.3 and 70.9 ppm; elemental analysis: $\text{C}_{20}\text{H}_{15}\text{NOS}_2$ requires C, 68.7; H, 4.3; N, 4.0. Found C, 69.1; H, 4.3; N, 4.0%. MS (EI) calculated mass 349.0595, measured mass 349.0602.

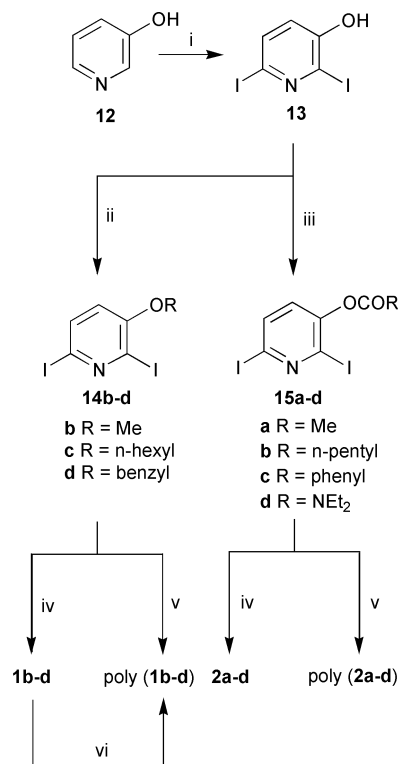
Results and discussion

Monomer synthesis

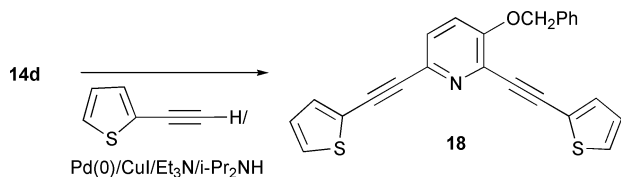
Our synthetic strategy is outlined in Scheme 1 and uses commercially available and inexpensive 3-hydroxypyridine **12** as the starting material. Our strategy was chosen so that the required polymers could be synthesised from appropriate monomer precursors using either electrochemical or cross-coupling methodology. Di-iodination of 3-hydroxypyridine **12** using a literature procedure¹⁴ gave 2,6-diiodo-3-hydroxypyridine **13** from which the ether derivatives **14b–d** and ester/carbamate derivatives **15a–d** were prepared by alkylation or acylation respectively.¹⁵ Stille coupling of compounds **14b–d** and **15a–d** with the stannylated thiophene **16** gave the corresponding teraryl derivatives **1b–d** and **2a–d**. The crude yields of teraryls from these Stille reactions were generally moderate and products were purified by chromatography and recrystallisation. Compound **1b** was also prepared from compound **14b** and 2-thienylmagnesium bromide in a nickel catalysed Kharasch type reaction with an improved yield. Compound **1a** was prepared by hydrolysis of compound **2a**. The alkyne analogue **18** of compound **1d** was also prepared (62% yield) from compound **14d** and 2-thienylethyne¹⁶ in a Sonogashira type reaction (Scheme 2).



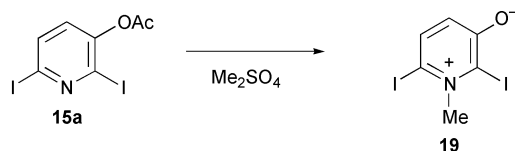
We have attempted to prepare the mesomeric betaine derivative **19** as shown in Scheme 3. Thus, when the acetate derivative **15a** was treated with dimethyl sulfate a mixture of products was obtained by ^1H NMR spectroscopy. *N*-Methylation and deacylation had apparently occurred (no carbonyl group was observed in the ^{13}C NMR spectra) but satisfactory microanalytical data and high resolution mass spectra could



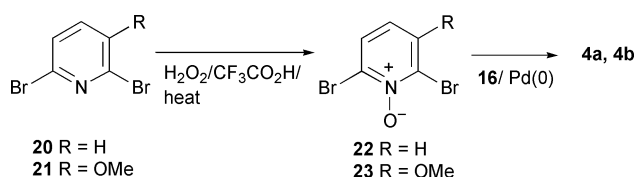
Scheme 1 Monomer and polymer synthesis. Reagents and conditions: i, aq. Na_2CO_3 -I₂; ii, RX -base; iii, ClCOR -base; iv, **16**-Pd(0); v, **17**-Pd(0); vi, cyclic voltammetry.



Scheme 2 Synthesis of compound **18**.



Scheme 3 Attempted synthesis of betaine **19**.



Scheme 4 Synthesis of *N*-oxides **4a** and **4b**.

not be obtained. Iodination of the heterocyclic mesomeric betaine **5** also failed to give compound **19**.

The *N*-oxide derivatives **4a** and **4b** were prepared as outlined in Scheme 4. Thus, treatment of 2,6-dibromopyridine **20** with aqueous hydrogen peroxide in hot trifluoroacetic acid afforded 2,6-dibromopyridine *N*-oxide **22** which underwent a Stille reaction with the stannylated thiophene **16** giving the desired product **4a**. By an analogous procedure, *N*-oxide **4b** was obtained from 2,6-dibromo-3-methoxypyridine **21** via 2,6-dibromo-3-methoxypyridine *N*-oxide **23**.

Chemical polymerisation reactions

Compounds **14b–d** and **15a–d** were reacted with the stannylated bithiophene derivative **17** to yield poly (**1b–d**) and poly (**2a–d**) respectively. The crude polymers obtained from these reactions were extracted with hot toluene (Soxhlet) to remove lower molecular weight material but the remaining higher molecular weight materials proved to be highly insoluble in a variety of solvents, even when they possessed long side chains *e.g.* poly (**1c** and **2b**). The UV spectra (ethanol) of the polymers were not particularly informative because there was not a clear cut-off point on the long wavelength absorption edge and this

precluded an accurate evaluation of the polymers' optical band-gaps. The polymers were relatively soluble in trifluoroacetic acid and the UV spectra of poly (**1c** and **2b**) were also determined in this solvent. These polymers showed λ_{max} at 531 nm and 494 nm respectively but we must bear in mind that in trifluoroacetic acid solution we are recording the spectra of protonated materials. The longest wavelength absorption edge in these two protonated polymers were well defined at 613 nm and 578 nm respectively indicating band-gaps of 2.0 eV for poly (**1c**) and 2.15 eV for poly (**2b**). The ^1H NMR spectra for the series of polymers (**1b–d** and **2a–d**) could be obtained in deuterated trifluoroacetic acid solution which confirmed their proposed structures. Microanalytical data on the chemically prepared polymers generally indicated lower than calculated percentages of carbon and nitrogen and this might reflect the presence of relatively short chains, possibly terminated with iodine.

When the *N*-oxides **22** and **23** were reacted with the stannylated bithiophene **17** only highly insoluble materials that gave UV spectra without well defined long wavelength absorption edges could be obtained. The ^1H NMR spectra of these materials in deuterated trifluoroacetic acid showed the presence of aliphatic protons indicating the presence of tributyltin residues and hence low molecular weight products are probably formed. This has been attributed to the lower reactivity of the bromo substituents in the Stille coupling reactions and, in the case of the *N*-oxide **23**, steric hindrance at the 2-position. These materials were not investigated further. In view of the insolubility of chemically prepared polymers our attention was directed at preparing the target polymers electrochemically.

Electrochemistry

The redox behaviour of compounds **1a–d**, **2a–d** and **18** were firstly characterised by cyclic voltammetry (*vs.* Ag/AgCl), using dichloromethane as the solvent and tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 200 mV s⁻¹. For the teraryl derivatives, two irreversible oxidation waves were observed between +1.09 and +1.99 V (Table 1), and there was a further single electron irreversible reduction process in the range -1.00 to -1.32 V. Whilst there was no apparent relationship between $E_{1\text{red}}$ and the nature of the substituents, there was a pronounced difference in the oxidation potentials between compounds **1b–d** bearing ether groups ($E_{1\text{ox}} = +1.34$ to +1.42 V) and those compounds **2a–d** possessing ester/carbamate functionalities ($E_{1\text{ox}} = +1.59$ to +1.73 V). The shift towards more positive potentials for compounds **2a–d** was attributed to a combination of: (i) steric hindrance between the bulky ester/carbamate group and the adjacent thiophene ring, which forces the heterocyclic rings out of coplanarity, and (ii) reduced electron donating effect of the ester/carbamate functionality

Table 1 UV and electrochemical data for compounds **1a–d**, **2a–d** and **18**.

Compound	Electrochemistry ^a			Absorption maxima/nm		Band-gap		
	$E_{1\text{ox}}$	$E_{2\text{ox}}$	$E_{1\text{red}}$	Monomer ^b	Polymer ^c	Optical	Electrochemical	Redox peaks, polymer/V
1a	+1.09	+1.56	-1.32	351	412, 602, 787	—	—	+1.14 ^d (76), -1.13
1b	+1.37	+1.90	-1.14	355	448	1.63 eV	1.39 eV	+1.10 ^d (50), -1.11
1c	+1.42	+1.75	-1.01	355	383, 408, 442	1.52 eV	1.63 eV	+1.14 ^d (213), -1.35
1d	+1.34	+1.46	-1.13	356	452	1.92 eV	1.55 eV	+1.10 ^d (143), -1.21
2a	+1.65	+1.94	-1.04	337	—	—	—	—
2b	+1.59	+1.99	-1.16	338	—	—	—	—
2c	+1.60	+1.95	-1.00	337	—	—	—	—
2d	+1.73	+1.97	-1.08	338	—	—	—	—
18	+1.54	+1.92	-1.11	354	—	—	—	—

^aExperiments carried out in dichloromethane, values given in V. ^bIn dichloromethane. ^cFilm on ITO glass. ^dReversible or quasi-reversible wave, $E^{1/2}$ given in V, $E_{\text{pa}} - E_{\text{pc}}$ (in mV) given in parentheses.

compared with that of the ether groups in compounds **1b–d**. Both these factors result in a less efficient π -electron donor system for derivatives **2a–d** and these electrochemical results concur with data obtained from electronic absorption studies: the values of λ_{max} for the ether-containing compounds **1b–d** are *ca.* 18 nm higher than those of the ester/carbamate analogues **2a–d** (Table 1). Interestingly, the cyclic voltammogram of the hydroxy system **1a** gave lower oxidation potentials compared with the alkoxy analogues **1b–d**. A reduction in steric hindrance in this case, coupled to an increase in planarity of the molecule, can not be invoked, since the absorption maximum for **1a** (351 nm) is the lowest in series **1**. It is possible that compound **1a** exists partially as its mesomeric betaine tautomer and consequently pyridoxy radicals are formed on oxidation.

The bis(thienylacetylene)pyridine species **18**, showed similar redox behaviour to the substituted dithienylpyridine derivatives. Thus, compound **18** gave two irreversible oxidation peaks at +1.54 V and +1.92 V, together with a single irreversible reduction signal at -1.11 V. Notably, the acetylene derivative **18** is a significantly weaker donor than the analogous dithienylpyridine **1d**. The difference between the values for $E_{1\text{ox}}$ and $E_{2\text{ox}}$ is 200 mV and 460 mV, respectively, yet the absorption maxima for the two compounds differ by only 2 nm.

The *N*-oxide derivatives **4a** and **4b** were not electroactive within the limits of the solvent.

Electropolymerisation

Electropolymerisation experiments were attempted for all compounds shown in Table 1 (dichloromethane, 10^{-3} M substrate, 0.1 M TBAPF₆, Ag/AgCl reference electrode). The procedure involved repetitive scanning over the second and/or first oxidation waves at a scan rate of 100 mV s^{-1} , using a gold disk or an indium–tin oxide (ITO) working electrode. The cyclic voltammograms representing polymer growth for each of the compounds in series **1** are shown in Fig. 1. None of the ester/carbamate derivatives **2a–d** or the acetylenic system **18** showed any signs of electrodeposition. Poly (**1a–d**) all exhibited

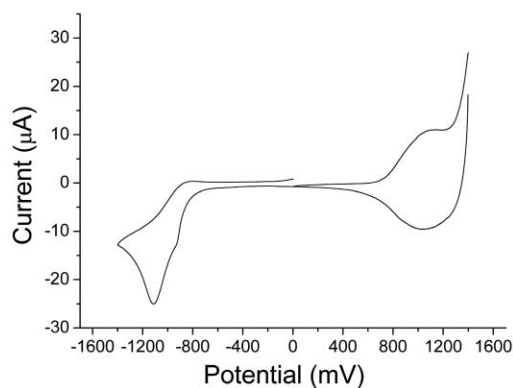


Fig. 2 Cyclic voltammogram of poly (**1b**) in monomer-free acetonitrile solution as a thin film on a Au working electrode (Ag/AgCl reference electrode, Pt counter electrode, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}).

similar redox behaviours: reversible/quasi-reversible oxidation waves were observed between +1.10 and +1.14 V, and irreversible reduction processes took place within the range -1.11 and -1.35 V. Fig. 2 depicts a representative cyclic voltammogram for the series. The relationship between the scan rate and peak current (E_{ox}) for all four polymers gave a linear fit ($R > 0.999$; Fig. 3). This indicated the stability of the polymers towards p-doping and confirmed that charge transport through the film is not diffusion limited (*i.e.* the electroactive polymer film behaves identically to a monolayer-derivatised electrode).¹⁷

The absorption maxima for poly (**1a**), poly (**1b**) and poly (**1d**) were red-shifted, compared to those of the corresponding monomers by 61 nm, 93 nm and 96 nm respectively. The difference is indicative of an increase in conjugation length of the polymer, compared to the monomer unit, which is typical for polythiophene species. The absorption spectrum for poly (**1c**) gave a major absorption peak at 383 nm, together with small shoulder peaks at 408 and 442 nm. Also, there was only a

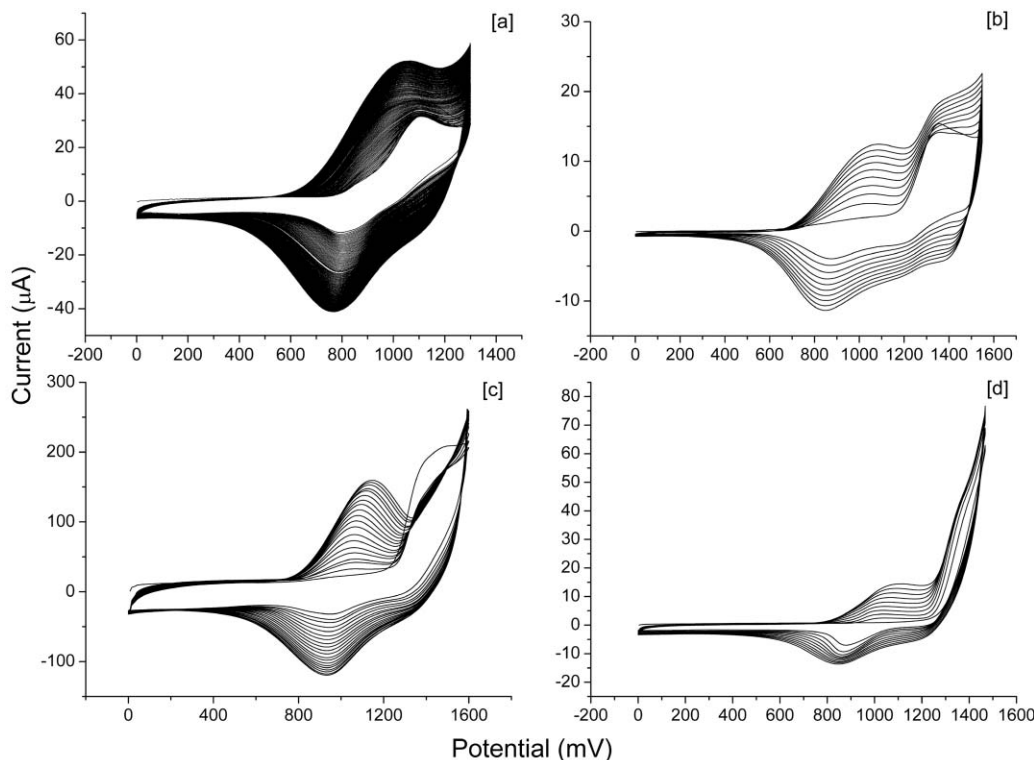


Fig. 1 Electrochemical polymerisation of **1a–d** on Au disk electrodes (Ag/AgCl reference electrode, Pt counter electrode, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}).

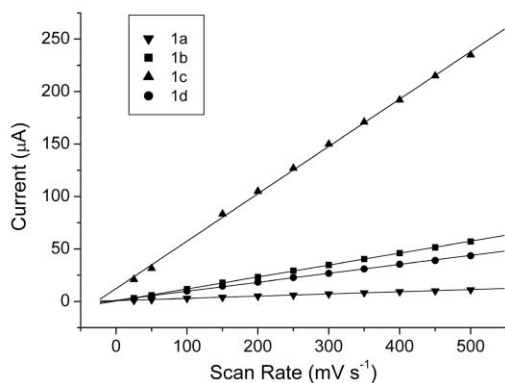


Fig. 3 Plot of current vs. scan rates for **1a–d**.

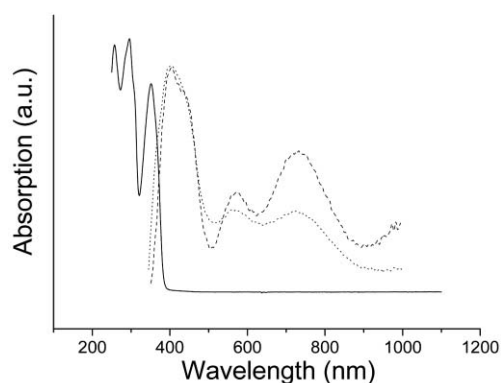


Fig. 4 Electronic absorption spectra of **1a** (—) (in dichloromethane) and poly (**1a**) (on ITO glass) after dedoping for 2 hours (---) and 5 hours (····).

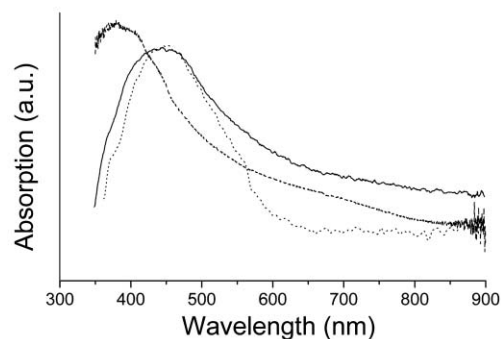


Fig. 5 Electronic absorption spectra of poly (**1b**) (—), poly (**1c**) (---) and poly (**1d**) (····) on ITO glass after dedoping.

small shift in λ_{max} for poly (**1c**) (28 nm); therefore, the polymer is most likely to be a short chain material with a high polydispersity.

The optical band-gap of a conjugated polymer can be deduced from the absorption spectrum by identifying the longest wavelength absorption edge. Electrodeposition on ITO glass of the four polymers was achieved under the conditions

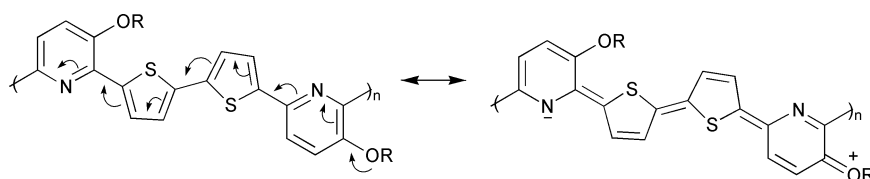


Fig. 6 Delocalisation in poly (**1b–1d**).

given above. As expected, the as-grown polymers were obtained in the oxidised state. The doped state of poly (**1a**) proved to be persistent, even after repetitive cycling over the range 0.1 V to -0.2 V for several hours. Fig. 4 shows the absorption spectra for the monomer **1a** and poly (**1a**) during the dedoping process. The maximum at 787 nm is indicative of chain oxidation, whereas that at 602 nm could be due to intramolecular charge transfer involving the mesomeric pyridinolate structure and the thiophene rings. Such a 'push-pull' mechanism would stabilise the oxidised state, giving good reason for the failure to dedope the polymer. After dedoping the remaining polymers (repetitive cycling over the range 0.1 V to -0.2 V for 2–5 hours), the absorption spectra were obtained for poly (**1b–d**) (Fig. 5). The band-gap (E_g) values are given in Table 1. Due to the doped state of poly (**1a**), the E_g for this material could not be deduced; however, it was found that the band-gap of poly (**1b**) was 0.29 eV lower than that of poly (**1d**), which is attributed to the increased steric effect of the bulkier benzyl ether substituent. Because of the postulated high polydispersity of poly (**1c**), the precise value of the absorption edge in this case is probably meaningless, since the longest chain system in the film is unlikely to represent a significant proportion of the material.

For each dedoped polymer, the electrochemical band-gap can be determined by the difference between the onset potentials for p- and n-doping (Table 1). Although the values are somewhat lower than the optical band-gaps, it is evident from the electrochemical data that poly (**1b**) bears a higher level of conjugation and coplanarity than poly (**1d**). The value for the electrochemical band-gap of poly (**1c**) when compared to the optical band-gap does not follow the same trend as for poly (**1b** and **1d**); for the reasons given above, this behaviour cannot be compared directly to the results obtained from poly (**1b** and **1d**).

The reasons for the relatively low band-gaps of poly (**1b–1d**) compared with polythiophenes are intriguing and may be a consequence of the delocalisation depicted in Fig. 6. These polymers might therefore be considered as 'charge transfer' polymers in which the oxygen lone pair is mesomerically associated with a pyridine ring further down the chain.

Conclusions

In conclusion, poly (**1b–d**) have been successfully prepared from teraryl precursors **1b–d** using electrochemical oxidation and deposited on ITO glass. These electrochemically prepared polymer films all exhibit lower band-gaps than typical polythiophenes indicating that an electron-rich pyridine ring can therefore usefully replace a thiophene ring in polythiophene analogues.

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