Functionalisation and Characterisation of Novel Conducting Polymer Interfaces

Karl S. Ryder,[a,b] **David G. Morris**[b] **and Jon M. Cooper***[a]

[a] *Bio-Electronics Research Centre, Department of Electronics & Electronic Engineering, Rankine Building, University of Glasgow, Glasgow, UK G12 8LT*

[b] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*

The synthesis and characterisation of novel β-substituted poly(pyrroles) derived from poly(I) (I = pentafluorophenyl 1*H*-pyrrole-3-acetate) and reactions of electrode-bound poly(I) with a variety of neutral nucleophiles, including 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose are described.

Poly(pyrroles) are often used as conducting interfaces because the substitution chemistry of the monomer is well defined, electrochemical polymerisation is easy, and the resultant polymers form robust and even films. For example poly(pyrroles) substituted with crown- and azacrown-ethers have recently been used in ion-selective electrodes,[1] with amino acid or peptide motifs for bioelectrochemical recognition and modelling,[2,3] and with carboxylic acid groups to promote direct electron-transfer to a redox protein.[4] In addition poly(pyrroles) have been used as a matrix for oxidase enzymes in amperometric biosensors and in olfactory arrays like the electronic nose.[5] Such systems are usually developed in two stages, firstly, the synthesis of an appropriate substituted pyrrole monomer, followed by electrochemical polymerisation.

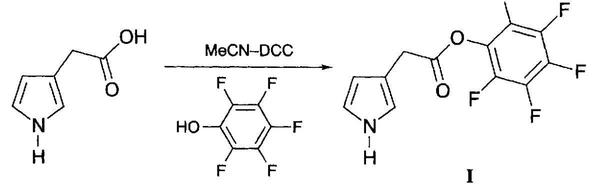
The limiting step is usually synthesis of the pyrrole monomers, which is often difficult and tedious.[4] This is especially true where substituents are placed at the β-positions, generally accepted as a prerequisite, for polymers with high electrical conductivity.[1,6] An alternative to this scheme is to introduce the desired functional groups onto a preformed polymer. This has two important advantages, (*i*) functional groups could be incorporated into the polymer that would otherwise either be destroyed by the oxidative conditions required for polymerisation, or interfere with the polymerisation process *e.g.* by attacking the pyrrole radical cation, and (*ii*) synthesis of only a single monomer is required as a route to a variety of functionalised polymers. Previously, covalent modification of pyrrole derivatives *after* polymerisation has rarely been successful because of poor reagent permeation of, and slow diffusion within the polymer film.[7] Characterisation of the resultant intractable polymers has also proved difficult.

In this paper we have sought to develop β-substituted poly(pyrroles) as precursors to novel highly conducting polymers functionalised with a variety of groups, including amino acids, for use in our studies on bioelectrochemical interfaces. We have used electrochemical methods, and a combination of specular reflectance FTIR and X-ray photoelectron spectroscopies to enable both interfacial and bulk characterisation of the substituted polymer.

Here we describe for the first time the synthesis and electrochemical polymerisation of pentafluorophenyl 1*H*-pyrrole-3-acetate, **I**. The pentafluorophenoxy group of this molecule is an excellent leaving group allowing facile functionalisation of the resultant polymer with a range of neutral nucleophiles including an amino acid and a chiral sugar derivative. Also, the fluorine atoms, present in the pentafluorophenyl substituent, act as a sensitive label for characterisation by X-ray photoelectron spectroscopy, (XPS).[9] We have been able to determine both the extent of heterogeneous substitution and, for the first time, to correlate the hydrophobic nature of the precursor polymer with its backbone electroactivity.

Pentafluorophenyl 1*H*-pyrrole-3-acetate was prepared, in high yield, from 1*H*-pyrrole-3-acetic acid and pentafluorophenol using dicyclohexylcarbodiimide, (DCC), according to Scheme 1.[†] The new molecule **I** was characterised by NMR and FTIR, showing the characteristic high energy carbonyl stretch at ν(C=O) 1784 cm^{-1}. All spectroscopic data were consistent with the formulation of **I**. Electrochemical polymerisation of **I** (17 mmol dm^{-3}), from MeCN or propylene carbonate solution (100 mmol dm^{-3} [NBu$_4$][ClO$_4$]), was facile on Au, Pt, and vitreous carbon electrodes at potentials close to 0.9 V *vs.* AgCl–Ag reference. The resultant, even, adherent films were dark brown in appearance and showed characteristic sharp absorbance bands in the specular reflectance FTIR spectrum at ν(C=O) 1785 cm^{-1}, and ν(C–F) at 1000 cm^{-1}. The XPS spectrum of a film of poly(**I**) (*ca.* 2 μm thick) formed on a Au coated glass slide also showed the presence of fluorine, with strong signals for O, N and C in appropriate proportions. From these data we conclude that the pentafluorophenyl ester group remains intact during the polymerisation process. This is in accord with previous observations on similar compounds substituted at the N-position.[10] Cyclic voltammetry of a 2 mm Au disk electrode coated with poly(**I**) (2mC cm^{-2}, growth charge), in fresh MeCN (100 mmol dm^{-3} [NBu$_4$][ClO$_4$]), showed a quasi-reversible oxidation associated with the doping/de-doping process of the poly(pyrrole) backbone.

Substitution of the pentafluorophenoxy groups throughout the polymer was achieved by soaking the polymer coated electrode in an MeCN solution of *e.g.* glycine ethyl ester, or the



Scheme 1

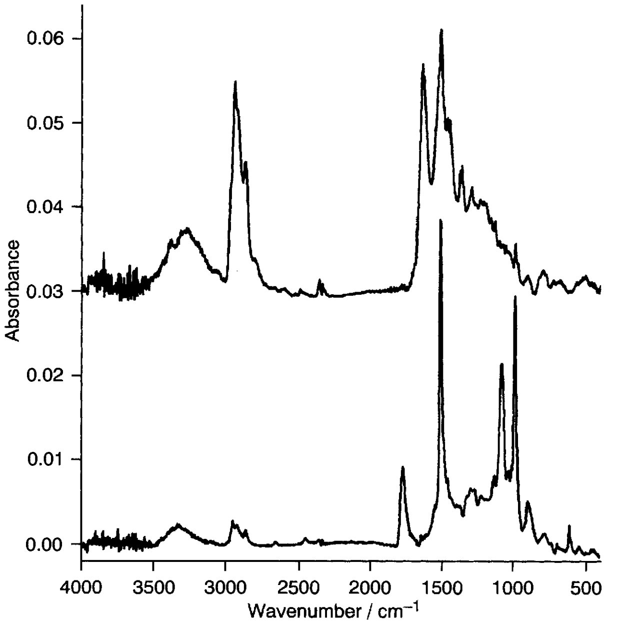


Fig. 1 Specular reflectance FTIR spectra of a sample of poly(**I**) (growth charge, 90 mC cm^{-2}, *ca.* 2 μm thick), before (bottom) and after (top) soaking for *ca.* 1 h in an MeCN solution of (1*R*)-(+)-*endo*-bornylamine (the top spectrum is offset by 0.03 absorbance units for clarity)

more sterically demanding (1*R*)-(+)-*endo*-bornylamine, for a period of *ca.* 1 h. The reaction in the polymer was monitored by specular reflectance FTIR, Fig. 1, which showed the shift of carbonyl stretch fom 1785 to 1644 cm^{-1} consistent with the formation of an amide bond. Also the complete loss (within a 5–10% detection limit) of the pentafluorophenoxy group from the polymer was evidenced by the disappearance of the band at 1000 cm^{-1} from the spectrum. Transesterification of poly(**I**) was also achieved by soaking in methanol, although the rate of reaction was slower than those of the amines as a consequence of the fact that methanol is a weaker nucleophile.

Samples of poly(**I**) were examined by XPS before and after exposure to (*i*) glycine ethyl ester, (*ii*) methanol, and (*iii*) water. Whereas the FTIR spectrum gives an averaged representation of the polymer composition (since the beam penetrates the film and is reflected from the surface of the Au substrate) throughout the film, XPS provides information only about the interfacial region (at a take off angle of 90° the collected photoelectrons emanate from a region < *ca.* 1 nm from the surface). XPS spectra of the samples exposed to methanol and glycine closely mirrored the FTIR data clearly showing a loss of fluorine, Fig. 2(*a*). Also the shape of the carbon signal is modified in accord with the loss of aromatic carbon atoms[9] after substitution of the pentafluorophenoxy group, Fig. 2(*b*).

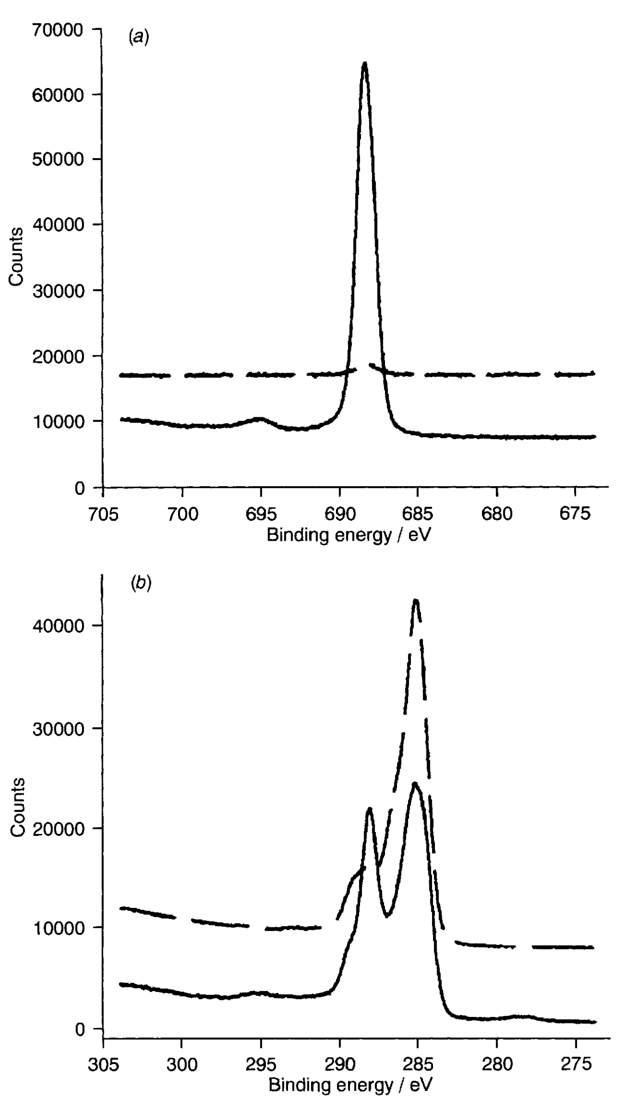


Fig. 2 X-Ray photoelectron spectra (at a contact angle of 90°, slit width = 0.5 mm) of polymer coated Au electrodes (growth charge, 90 mC cm^{-2}, *ca.* 2 μm thick). The solid lines represent spectra of poly(**I**) precursor, the dotted lines show spectra of the same polymer after soaking for 1 h in an MeCN solution of glycine ethyl ester, (*a*) fluorine lines, (*b*) carbon lines.

Contrary to expectation, samples of poly(**I**) did not show rapid hydrolysis when exposed to water, the FTIR spectrum of the polymer was unchanged after soaking in water for 12 h. However, the fluorine signal detected by XPS was greatly diminished. This strongly suggests that water cannot permeate into the bulk of the film and that only the outer surface, which is exposed to the aqueous environment, undergoes hydrolysis. The hydrophobic nature of poly(**I**) is confirmed by the lack of electroactivity in aqueous electrolyte, determined by CV, compared to that of the same polymer in MeCN, Fig. 3; this is presumably because of the inability of the hydrated ClO_4^- counterions to permeate the polyfluorinated membrane. To our knowledge this is the first example where the attenuated electroactivity of the polymer backbone is directly correlated with the hydrophobic nature of the polymer, as demonstrated by XPS measurement.

To emphasise the scope of this approach to functionalised conducting polymers we exposed an electrode coated with poly(**I**) to the chiral sugar derivative 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose. After a period of several hours the electrode was removed and rinsed with fresh MeCN; subsequent FT-IR analysis showed the substitution reaction was complete. The electrochemical response of the sugar-derivatised polymer electrode was then examined in MeCN solutions of (1*S*)-(+)- and (1*R*)-(−)-10-camphor sulfonic acid under identical conditions, Fig. 4. The chiral polymer electrode clearly shows a degree of selectivity for the (1*S*)-(+)-10-camphor sulfonate anion, although the magnitude of voltammetric response is smaller than that for the less bulky ClO_4^- counterion. Integration of the voltammetric curves indicates that 4 equivalents of (1*S*)-(+)-counterions are incorporated into the polymer film for every equivalent of the (1*R*)-(−)- enantiomer. This result compares favourably with an earlier report of a similar system fabricated from a polymer of **II**, an N-substituted pyrrole adduct of the same sugar derivative.[11] However, here the enantioselectivity was in the opposite sense *i.e.* the (1*R*)-(−)-enantiomer was favoured.

In conclusion, we have demonstrated a route to a range of new β-substituted poly(pyrroles) *via* a single precursor polymer. The scope of this approach is wide ranging since

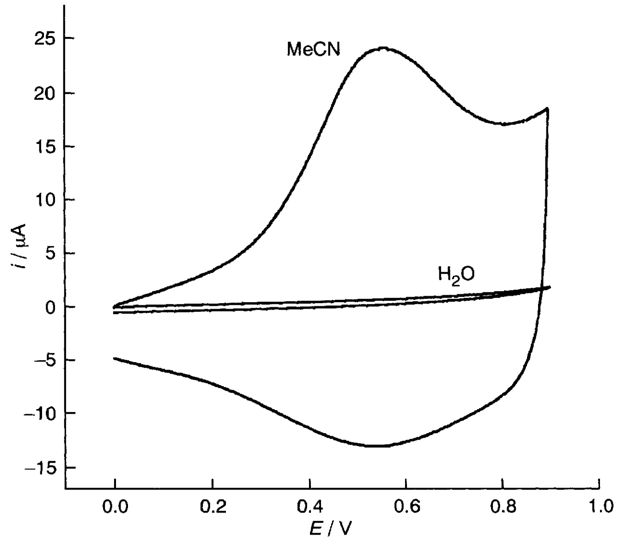


Fig. 3 CV of a 2 mm Au disk electrode coated in poly(**I**) (polymerised from a 14 mmol dm^{-3} MeCN solution of (**I**), 100 mmol dm^{-3} [NBu_4][ClO_4], growth charge 2 mC cm^{-2}), in a 100 mmol dm^{-3} [NBu_4][ClO_4] MeCN solution, and in 100 mmol dm^{-3} [Li][ClO_4] aqueous solution. The potential scan rate for both voltammograms was 50 mV s^{-1}, and the potential was measured relative to a AgCl–Ag reference electrode.

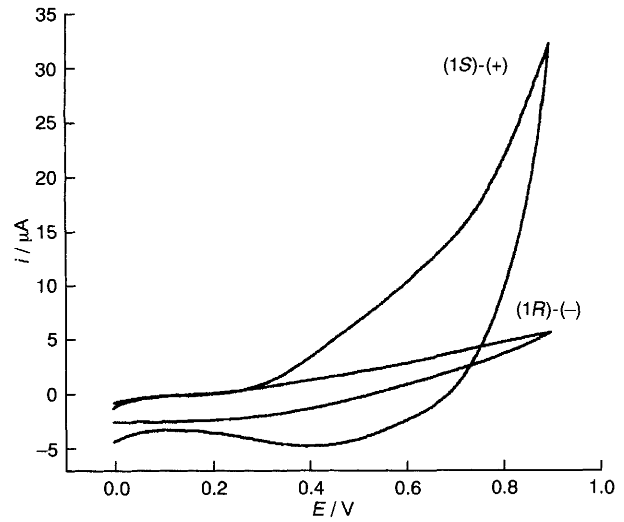
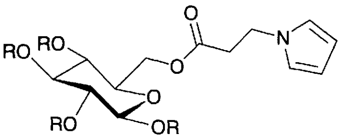


Fig. 4 CV of a planar Au electrode coated (0.8 cm^2) in poly(**I**) (polymerised from a 17 mmol dm^{-3} MeCN solution of **I**, 100 mmol dm^{-3} [NBu$_4$][ClO$_4$], growth charge 90 mC cm^{-2}) presoaked in an MeCN solution of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose for 12 h and then rinsed thoroughly in fresh MeCN. The curves show the voltammetric responses of the electrode in 100 mmol dm^{-3} MeCN solutions of (1*S*)-(+)-, and (1*R*)-(−)-10-camphor sulfonic acid (ν = 25 mV s^{-1}, the potential was measured relative to a AgCl–Ag reference electrode).



II R = C(O)Me

substitution of poly(**I**) is facile, and does not require time consuming and difficult synthetic methods for the preparation of each new polymer, also quantities of reagents required are vanishingly small. Finally, this approach may be particularly useful in the fabrication of conducting polymer sensor arrays, such as those used in artificial olfactory systems, where consistency of growth conditions is beneficial. Individual functionalisation of the elements in an array, from a common precursor polymer, will be possible.

The authors gratefully acknowledge the EPSRC for financial support, grant No's: GR/K00721, and GR/H65382, also the ESPRIT programme 7282 (TOPFIT), Dr A. Glidle, Dr G. Beamson and Dr F. Garnier (NRS) for valuable help and discussion.

Received, 13th April 1995; Com. 5/02401C

Footnote

† 1*H*-pyrrole-3-acetic acid was prepared from 1-phenylsulfonyl-3-acetyl pyrrole using Tl^{III}(NO$_3$)$_3$·3(H$_2$O) by the literature method.[8]

References

1 H. Kori-Youssoufi, M. Hmyene, F. Garnier and D. Delabouglise, *J. Chem. Soc., Chem. Commun.*, 1993, 1550.
2 F. Garnier, H. Kori-Youssoufi, P. Srivastava and A. Yassar, *J. Am. Chem. Soc.*, 1994, **116**, 8813.
3 C. J. Pickett, K. S. Ryder and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1992, 694.
4 J. M. Cooper, D. G. Morris and K. S. Ryder, *J. Chem. Soc., Chem. Commun.*, 1995, 697.
5 J. W. Gardner, *Microsensors Principles and Applications*, Wiley, New York, 1994.
6 J. R. Reynolds, P. A. Poropatic and R. L. Toyooka, *Macromolecules*, 1987, **20**, 958; R. Casas, A. Dicko, M. Ribo, M. A. Vallés, N. Forrer-Anglada, R. Bonnett, N. Hanly and D. Bloor, *Synth. Met.*, 1990, **39**, 275.
7 A. F. Diaz and K. K. Kanazawa, *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1983, vol. 3.
8 A. Ho-Hoang, F. Fache, G. Boiteux and M. Lemair, *Synth. Met.*, 1994, **62**, 277.
9 G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers. The SCIENTA 300 Database*, Wiley, New York, 1992.
10 C. J. Pickett and K. S. Ryder, *J. Chem. Soc., Dalton Trans.*, 1994, 2181.
11 J.-C. Moutet, E. Saint-Aman, F. Tran-Van, P. Angibeaud and J.-P. Utile, *Adv. Mater.*, 1992, **4**, 511.