Merrifield chemistry on electropolymers: protection/(photo)deprotection of amine functions

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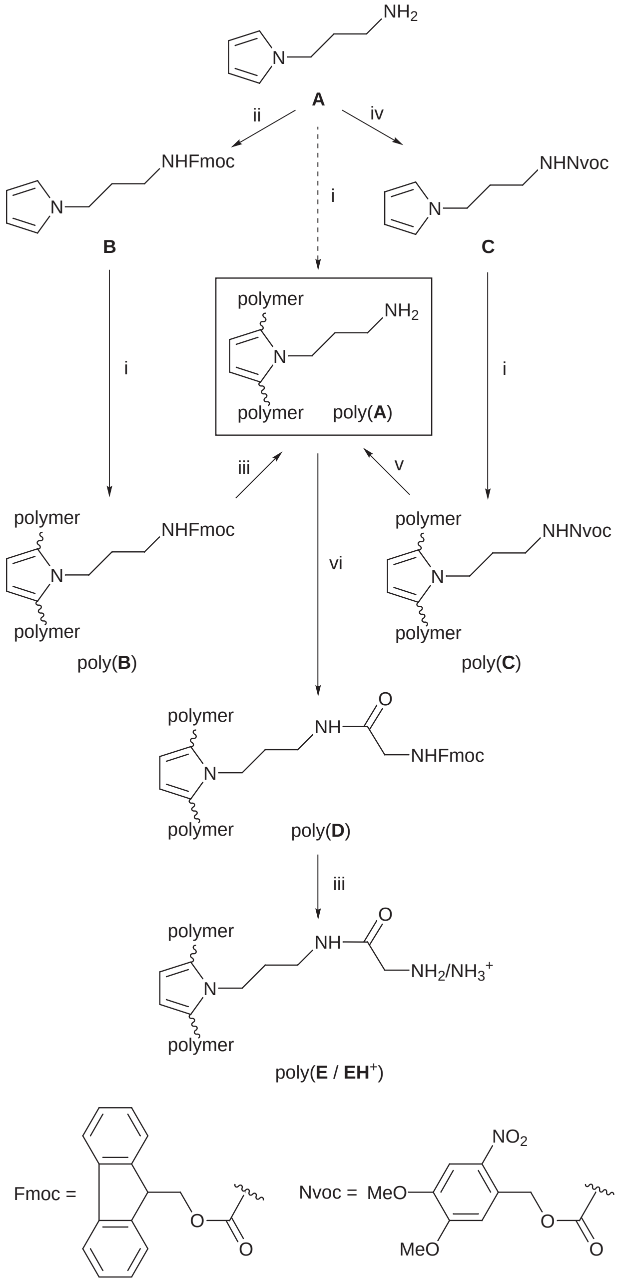
Amine protection/(photo)deprotection strategies allow functionalisation of electrode bound poly(pyrrole) films *via* reactions with active esters.

Polymers with substituent groups covalently anchored along the conjugated backbone of poly(pyrrole) or poly(thiophene) constitute a class of hybrid materials possessing potentially interactive electrical and molecular domains. They are consequently receiving considerable attention for sensing, electrocatalysis and other applications.[1–3] For example, a change in the redox response of an oligonucleotide functionalised pyrrole occurs upon recognition (binding) of a strand of complementary DNA.[3] The range of materials that can be made, and also aspects of their microfabrication, have been somewhat circumscribed by the need to synthesise and electropolymerise the appropriately substituted pyrrole or thiophene *monomer*.[4] This is problematic in cases where the desired substituent group is sensitive to the oxidative conditions of electropolymerisation or where the substituent is an inhibitor of this process. We have shown that one way in which such problems can be overcome is by *post-polymerisational modification* of pre-formed electropolymers which possess active ester groups.[4] The desired substituent groups are covalently attached to the polymer by amide or ester bond formation, and this general approach has been successfully adapted by others.[5] The converse derivatisation, reaction of *amine functionalised electropolymers* with active esters, could provide a complementary strategy for electropolymer functionalisation. This has the attraction that well-established protocols for solid-phase amine chemistry that have been developed on Merrifield resins might be adapted to electropolymers.[6] Herein we describe some first steps in this direction (Scheme 1).

Anodic oxidation of 3-pyrrol-1-ylpropylammonium cation **AH**$^+$ (Pt or vitreous carbon, 0.2 M [NBu$_4$][BF$_4$]–MeCN) gives the electroactive polymeric film poly(**AH**$^+$). The electropolymer can be (reversibly) deprotonated to give the free amine form, poly(**A**) but is otherwise quite unreactive: pentafluorophenolate active esters fail to modify bulk films of poly(**A**). Penetration of the film by the reagent is presumably prevented by close-packing of the polymer chains.

The problem is overcome by generating amine groups within the polymer from *N*-protected precursors. Fluoren-9-ylmethoxycarbonyl (Fmoc) and 6-nitroveratryloxycarbonyl (Nvoc) derivatised monomers **B** and **C** were synthesised from **A** (Scheme 1). Both of the *N*-protected monomers undergo facile electropolymerisation, as typified by the potentiodynamic growth of poly(**C**) (Fig. 1). Base deprotection of poly(**B**) or photodeprotection of poly(**C**) gives poly(**A**) (Scheme 1), as illustrated by the FTIR sprecta shown in Fig. 2.

In contrast with the inertness of poly(**A**) produced directly by electrooxidation of **A**, the amino polymer generated by *either* deprotection route readily forms amide derivatives upon reaction with pentafluorophenolate active esters. For example, diffuse reflectance FTIR spectroscopy shows that poly(**A**) formed by photolysis reacts with Fmoc-glycine pentafluoro-



Scheme 1 *Reagents and conditions*: i, MeCN, 0.2 M [NBu$_4$][BF$_4$], 5 mM **AH**$^+$; ii, FmocCl, Na$_2$CO$_3$, dioxane–water (1 : 1), 12 h, 22 °C; iii, 30% piperidine–MeCN, 1 h, room temp.; iv, NvocCl, Na$_2$CO$_3$, dioxane–water (1 : 1), 12 h, 22 °C; v, irradiation of 1 μm film for 4 h in 1% HBF$_4$·2Et$_2$O–MeCN using 30 W mercury UV/pyrex filter transmitting through 1 cm of solvent under nitrogen; vi, 25 mM Fmoc-glycine pentafluorophenolate ester in 12% Et$_3$N–MeCN, room temp., 4 h

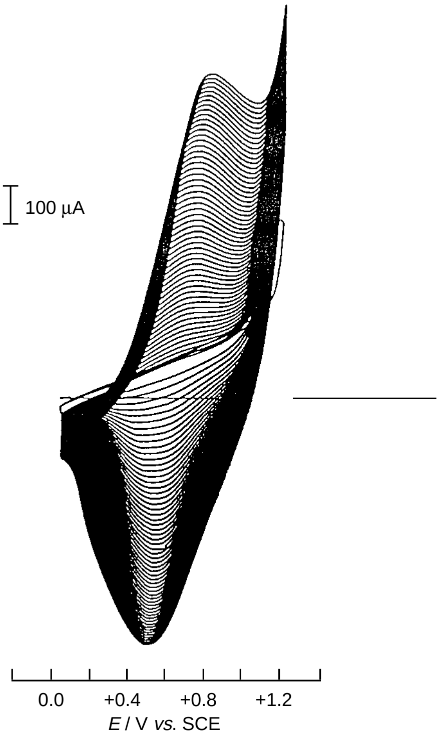


Fig. 1 Potentiodynamic growth of the Nvoc protected polymer, poly (**C**). The polymer was grown on a polished Pt disc electrode of radius 0.32 cm by cycling the potential between 0.0 and 1.20 V *vs.* SCE at 50 m V s^{-1} in 0.2 M [NBu_4][BF_4]–MeCN–5 mM **C**.

phenolate (Fig. 2). Moreover, this Fmoc-glycine-derivatised film, poly(**D**), can in turn be chemically deprotected with piperidine to unmask the fresh terminal amine groups of poly(**E**).

The difference in polymer reactivity clearly lies with access to the amine groups and is explained by deprotection affording molecular cavities around these groups and/or the relatively bulky Fmoc and Nvoc groups producing a more open polymer network.

Although the deprotection pathways lead to a decrease in conductivity, as judged from the redox response of the polymer backbone, optimisation of the deprotection conditions and/or the use of protected 3-substituted pyrroles may be expected to lead to enhanced conductivity.

In conclusion, we have shown that an amine-functionalised electropolymer based on an N-substituted poly(pyrrole) can be made either directly or by chemical or photochemical deprotection routes. The deprotection routes afford polymers which react with active esters to form amides, whereas the directly synthesised amino polymer is unreactive under the same conditions. Finally, we note that (i) the chemical and photolytic deprotection strategies offer a means of *patterning* electropolymers with arrays possessing differing molecular functions,[7] (ii) 'cavity formation' by amine deprotection/photodeprotection might provide a means for molecular *imprinting* of an electropolymer,[8] and (iii) successive protection/deprotection/peptide bond formation cycles (Merrifield chemistry) can be performed on electropolymers.

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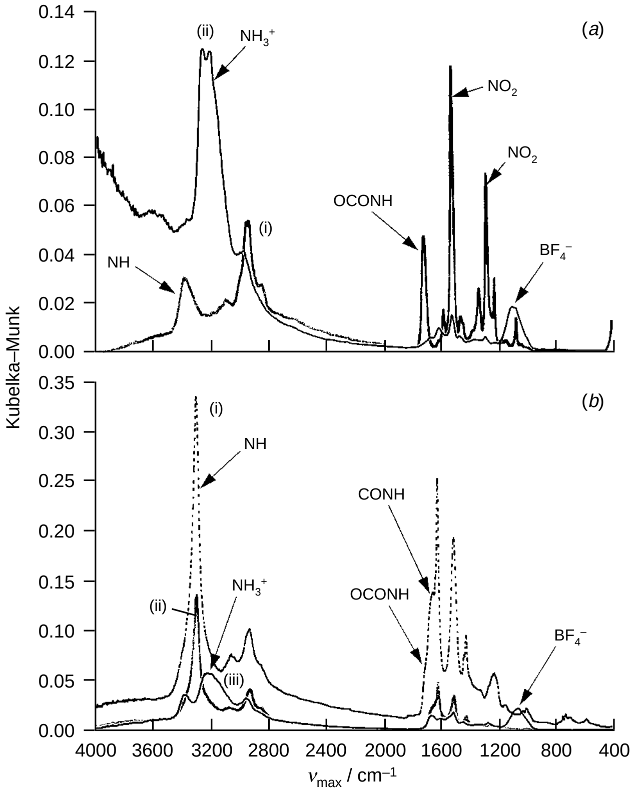

Fig. 2 (*a*) Diffuse reflectance FTIR spectra of (i) the Nvoc protected poly(**C**) and (ii) deprotected alkylammonium poly(**AH**$^+$) produced by photolysis of poly(**C**). (*b*) Diffuse reflectance FTIR spectra of (i) the Fmoc-glycine derivative, poly(**D**), formed by treating the poly(**A**) modified electrode with Fmoc-glycine pentafluorophenolate ester, (ii) the deprotected poly(**D**), which gives the amine film poly(**E**) by removal of Fmoc with piperidine, and (iii) the alkylammonium film poly(**EH**$^+$) formed by protonation of poly(**E**) (1% v/v $HBF_4 \cdot 2Et_2O$ in MeCN). Modifying the groups within the polymer changes the diffuse reflectivity characteristics of the film and thus relative band intensity *between* spectra.

Notes and References

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