

Control of the Lipophilicity of Polypyrrole by 3-Alkyl Substitution

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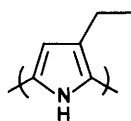
3-Alkyl substitution of the polypyrrole monomer leads to highly conductive and electroactive polymers and permits control, to a large extent, of their hydrophobic character.

The low value of the oxidation potential of polypyrrole [$E_{\text{ox}} = -0.1$ V/standard calomel electrode (SCE)] and the good environmental stability of its oxidised conducting state, have raised considerable interest over recent years.¹ As a consequence, a large number of studies have been devoted to the controlled modification of the polymer properties, whether by varying the characteristics of the incorporated anion,² or by chemical modification of the pyrrole monomer. Up to now, substitution of the nitrogen atom has been mainly used and has allowed the synthesis of polymers containing redox mediators or ligands for further complexation with transition metals.³ However, this *N*-substitution leads to a steep decrease in the conductivity ($\sigma < 10^{-3}$ S cm⁻¹),⁴ and also to an increase in the oxidation potential of the resulting polymer ($E_a > 0.6$ V/SCE).^{3,4} Some authors have pointed out that 3 or 3,4 substitution of the polypyrrole monomer has a much lower effect than *N*-substitution, on the conductivity of the resulting

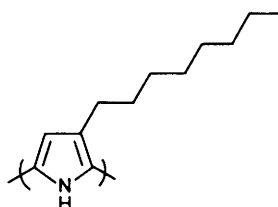
polymer.⁵ In previous studies devoted to polythiophene, we have already shown the large potential interest of 3-substitution. We demonstrated that by means of an alkyl spacer of appropriate length, even a bulky chiral centre can be grafted onto the 3-position, leading to a highly conducting and electroactive functionalised polymer.⁶

We demonstrate here how the lipophilic character of a conducting polypyrrole can be tuned by using an alkyl substituent of appropriate length, at the 3-position. The substituted monomers were prepared according to known procedures: *N*-tosylation of pyrrole,⁷ selective acylation in position 3 of the *N*-tosylpyrrole and subsequent hydrolysis of the tosyl group⁸ and reduction of the 3-acyl pyrroles.⁹

The electrochemical polymerisation of 3-alkylpyrroles in the conditions used for unsubstituted pyrrole (in propylene carbonate; NBu₄BF₄ 0.05 M; monomer 0.1 M; 0.6 V/Ag₂Ag⁺ 0.1 M MeCN) leads to homogeneous films. Their dc conductivity, measured by the four-probe method, is at least three orders of magnitude higher than that of the corresponding *N*-alkyl substituted polypyrroles:⁴ poly(3-ethyl pyrrole) (1), $\sigma = 6$ S cm⁻¹; poly(3-octyl pyrrole) (2), $\sigma = 2$ S cm⁻¹. Furthermore the oxidation potential of poly(3-alkylpyrroles) is comparable to that of polypyrrole: $E_a = -0.3$ V/Ag₂Ag⁺, or 0 V/SCE. Their electrochemical redox properties have been



(1)



(2)

Table 1. Quantity of charge exchanged during oxidation of polypyrrole and poly(3-alkyl pyrrole). The quantity of charge is referred to the number of monomer units in the polymer film, assuming a 100% electropolymerisation yield and 0.25 charge by monomer unit in the as-grown polymer.

Electrolyte 0.1 M	Polypyrrole	(1)	(2)
KCl/H ₂ O	23%	10%	0%
NBu ₄ BF ₄ /MeCN	11.5%	16%	20.8%
NBu ₄ CF ₃ SO ₃ /MeCN	4.6%	19%	19%
NBu ₄ TsO/MeCN ^a	0%	4.6%	22%

^a Ts = *p*-MeC₆H₄SO₂.

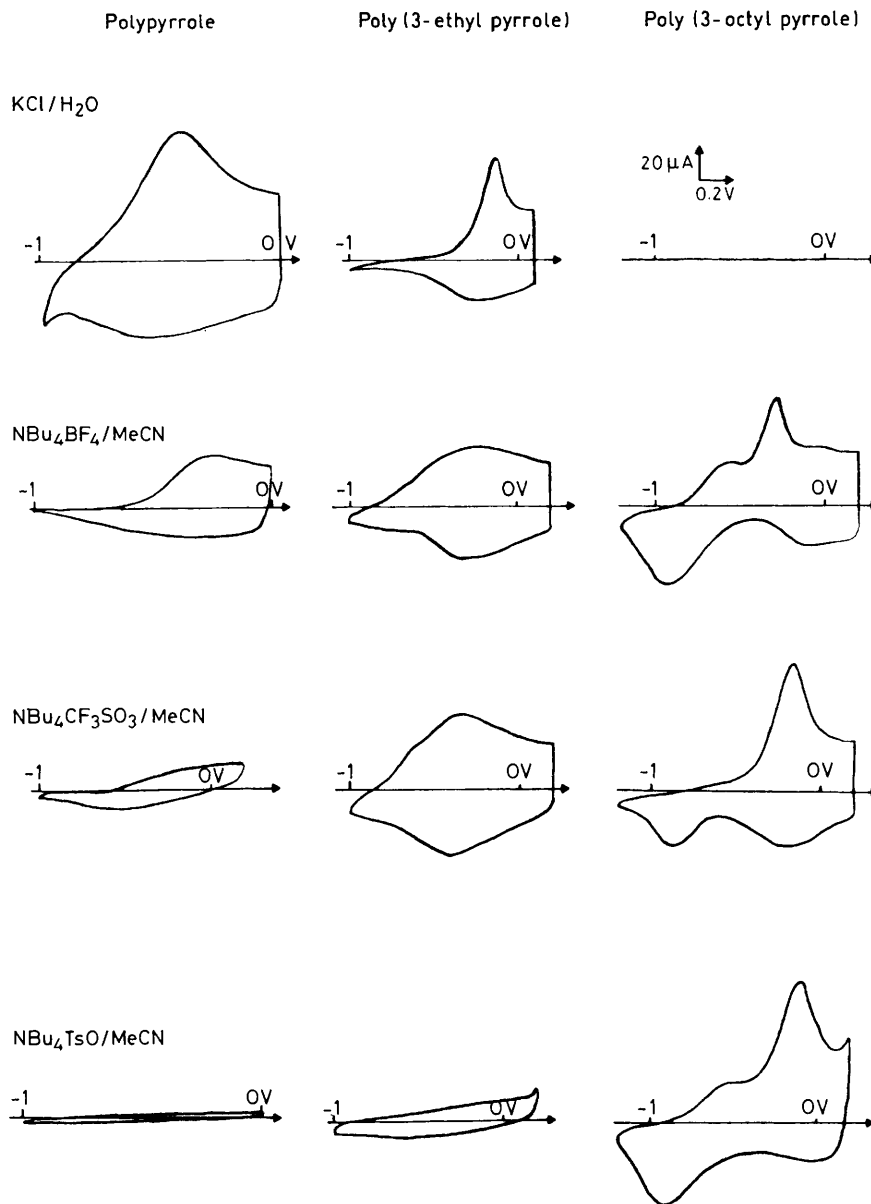


Figure 1. Cyclic voltammograms of polypyrrole and poly(3-alkyl pyrrole). Sweep rate 50 mV/s; Reference electrode: Ag/AgNO₃ 0.1 M MeCN; Electrolyte 0.1 M; Pt anode; Polymerisation charge: 0.1 C/cm².

analysed by cyclic voltammetry, using electrolytes of increasing lipophilicity (LiClO₄, NBu₄BF₄, NBu₄CF₃SO₃, NBu₄TsO in H₂O and MeCN).

The unsubstituted polypyrrole is fully electroactive in water but shows a decreasing electroactivity (expressed by the amount of charge reversibly exchanged upon redox cycling) when increasing the lipophilicity of the electrolyte (1st column on Figure 1 and Table 1; the data in Table 1 are constant on slower potential sweep rate excluding a kinetic effect). In contrast, poly(3-ethyl pyrrole) exhibits in water, an electroactivity half that of polypyrrole, but an increased exchange charge in organic medium, when increasing the lipophilicity of the electrolyte, except for the tosylate anion (2nd column on Figure 1 and Table 1). This latter result could be due to the size effect of big anions. Poly(3-octyl pyrrole) is not swelled by water and remains completely inactive in aqueous medium. This result shows that by substituting an alkyl chain of sufficient length, at the 3-position of the monomer, the

hydrophilic character of the polypyrrole backbone can be overcome. In contrast, in organic medium, the poly(3-octyl pyrrole) is fully electroactive and exhibits a second redox system at lower potential (3rd column on Figure 1 and Table 1). The appearance of this second redox system is related to the nature of the cation as evidenced by voltammetric analysis in lithium salts (Figure 2). It is now well established that the redox process of polypyrrole is accompanied by both the transport of electrolyte anion and cation.¹⁰ Shimidzu and co-workers have also observed two redox systems by voltammetric analysis of a polypyrrole synthesised with an alkyl sulphonate salt.¹¹ The effect they observed is explained by an anion trapped in the polymeric matrix which induces a cation movement. In a different way, the effect described here, arises from a specific affinity between the lipophilic polymer and lipophilic cations.

These results allow us to develop the concept of compatibility between a conjugated polymeric chain and its chemical

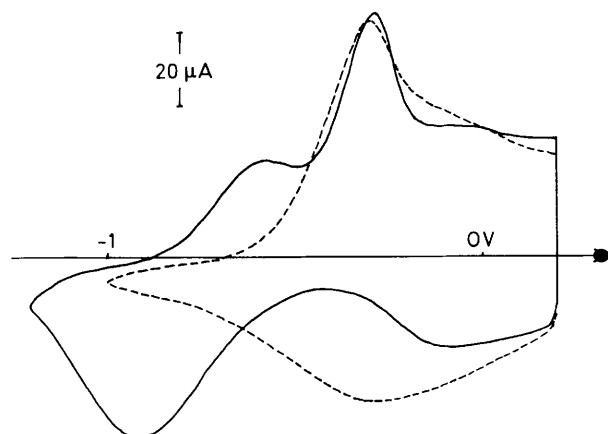


Figure 2. Cyclic voltammograms of poly(3-octyl pyrrole) in $\text{LiClO}_4/\text{MeCN}$ (---) and in $\text{NBu}_4\text{BF}_4/\text{MeCN}$ (—). Same conditions as for Figure 1.

environment. This approach appears to be essential for the development of specific electroactive membranes.¹² Selectivity or effectiveness towards organic species can be tuned by controlling the lipophilic character of the polymer membrane.

In conclusion, the functionalisation of conducting polypyrrole by substitution at the 3-position is of much wider potential use than the largely developed *N*-substitution. Without any dilution of the function in a copolymer, the poly(3-alkylpyrroles) show high conductivities (three orders of magnitude higher than that of their *N*-substituted homologues) and the same electroactivity as polypyrrole itself. Furthermore, this molecular control of the polypyrrole properties permits a monitoring of the lipophilic character of these conducting polymers.

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