Functionalization of polypyrroles with acids and β-diketones as complexing groups. Part 1: electrochemical synthesis and properties

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The synthesis of pyrroles functionalized by complexing groups such as acetylacetone, dibenzoylmethane or carboxylic acids is described, as well as their electrooxidation into functionalized polypyrroles. We have studied the behavior of poly(functionalized pyrrole) films in the presence of Li^+, Ni^{2+} and Co^{2+} cations by cyclic voltammetry (CV) and infrared (IR) spectroscopy. The electrochemical response under various conditions differs with the nature of the complexing group. We have also demonstrated the possibility to electrochemically generate copolymers with pyrrole and each functionalized pyrrole. The proportion of functional groups in the copolymers was estimated by following the peak potential dependence in cyclic voltammetry and was confirmed by IR spectroscopy.

In the past few years the preparation of conducting polymers bearing pendant groups and having tunable properties has aroused much interest due to their (potential) applications, especially in the field of electrochemical sensors, but also for electrocatalysis, ion extraction or corrosion protection.[1–5] Pyrrole polymers are of particular interest because their polymerization is easy, either by electrochemical[6,7] or chemical[8,9] methods. Polypyrroles bearing crown ethers, azamacrocycles, open chain nitrogen-containing ligands and benzo-15-crown-5 have been described by several groups[10–14] and have been shown to display tunable electrochemical properties in the presence of, for example, lithium or cobalt ions.

We have prepared pyrrole monomers bearing, as pendant groups linked to the pyrrole nitrogen, acetylacetone (ACAC), dibenzoylmethane (DBM) or carboxylic acid (CA) moieties, which are classically known as good cation complexing groups in solution. In addition, these groups are known to act as adhesion promoters on oxide layers.[15,16] The classical electropolymerization of the functionalized pyrroles as well as the electrochemical properties of the polymers have been studied. The complexing properties of such polymers towards metal ions have been investigated. The electrochemical properties of the CA functionalized polymers have been also found to change with the protonation state of the film. Copolymers of the functionalized monomers with pyrrole have been prepared, and the relative proportion of the functionalized species in the film is related to that in the polymerization feed.

Experimental

Methods

Melting points were measured with an IA 9200 apparatus. Infrared (IR) spectra were obtained between 600–4000 cm^{-1} (resolution 4 cm^{-1}) on a Bruker Spectrospin IFS-45 spectrometer on KBr pellets of the crushed samples. The polymer samples were obtained by scraping thin polymer film from an ITO electrode (2 cm^2). Ultraviolet-visible (UV-vis) spectra were recorded on a Beckman DU 520 UV-vis spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 200 MHz for ^1H and 50 MHz for ^{13}C on a Bruker Spectrospin AC 200 spectrometer.

Synthesis of the monomers

While the preparation of CA pyrroles through another route has been described,[17,18] we have chosen to prepare them by hydrolysis of the nitrile, which has the advantage of operating in basic conditions and avoids the use of acetic acid. The monomers have been prepared by a common strategy, which is summarized in Scheme 1. The ACAC or DBM functionalized pyrroles have been prepared by substitution of the corresponding ACAC or DBM anion on the ω-halohexylpyrroles or *N*-tosyloxyhexylpyrroles. It should be noted that the substitution reaction is unfortunately not straightforward in this latter case, due to the less favorable nucleophilic character/basic character balance of the diketonates, and that some elimination took place, which lowers the synthesis yields. Despite this drawback, appreciable quantities of products could be obtained by applying this synthetic scheme.

6-(Pyrrol-1-yl)hexanol **2** and *N*-(ω-tosyloxyhexyl)pyrrole **3** were synthesized by the method of Bidan.[19,20] The procedure was repeated without modification and NMR and IR data were in accordance with that reported.

***N*-(6-Bromohexyl)pyrrole (5a) and *N*-(10-bromodecyl)pyrrole (5b). 5a**: The reaction was carried out under nitrogen and in dry conditions. Pyrrolylpotassium salt **1**[19] (0.100 mol) was dissolved in 20 mL of DMSO. To a three-necked flask was introduced 0.120 mol of 1,6-dibromohexane in 50 mL of THF. Then **1** was slowly added (to permit heat elimination and avoid disubstitution). After 10 min stirring, the solution was poured into 500 mL of a saturated aqueous solution of

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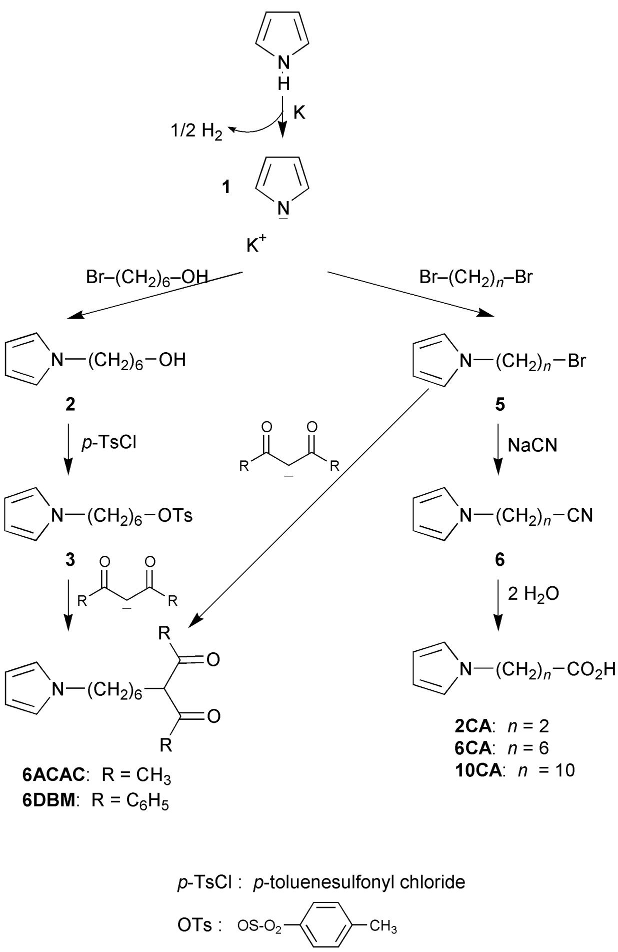

Scheme 1 Synthetic route for the functionalization of pyrrole by β-diketone (**6ACAC**, **6DBM**) and carboxylic acid (**2CA**, **6CA**, **10CA**) groups.

sodium sulfate and was extracted several times with diethyl ether. Solvents and pyrrole in the organic phase were removed under reduced pressure at 80 °C. The crude oil was purified by chromatography on silica gel with a solution of 5% diethyl ether–95% petroleum ether as eluent. Yield = 40–45%. ^{1}H NMR (CDCl$_3$): δ 1.35–2.00 (m, 8H); 3.45 (t, J = 6.7 Hz, 2H); 3.90 (t, J = 7.1 Hz, 2H); 6.15 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H).

5b: Same procedure as for **5a**, using 1,10-dibromodecane instead of 1,6-dibromohexane. ^{1}H NMR (CDCl$_3$): δ 1.30–1.85 (m, 16H); 3.40 (t, J = 6.8 Hz, 2H); 3.90 (t, J = 7.1 Hz, 2H); 6.15 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H).

3-[6-(Pyrrol-1-yl)hexyl]-2,4-pentanedione (6ACAC) and 1,3-diphenyl-2-[6-(pyrrol-1-yl)hexyl]-1,3-propanedione (6DBM). 6ACAC: To a solution of 0.0287 mol of potassium *tert*-butoxide in 5 mL of DMSO was first added 0.0287 mol of 2,4-pentanedione and then 0.0143 mol of **3** or **5a**. The reaction was carried out under nitrogen and in dry conditions. The mixture was heated at 90 °C for 2.5 h. The solution was then allowed to cool before being neutralized with hydrochloric acid (0.1 M) and the product was extracted with diethyl ether. The organic phase was washed several times with distilled water and dried on anhydrous sodium sulfate. The crude product was purified by chromatography on silica gel (5% diethyl ether–95% petroleum ether as eluent). Yield = 22%. IR: 3110 $\nu(\mathrm{C_{sp^3}-H})$; 2932 and 2865 $\nu(\mathrm{C_{sp^3}-H})$; 1710 cm^{-1} $\nu(\mathrm{C{=}O})$. ^{1}H NMR (CDCl$_3$): δ 1.20–1.90 (m, 8H); 2.1 (s, enol and diketone); 2.2 (s, enol), 3.50 (t, J = 7.2 Hz, diketone) 3.85 (t, J = 7.1 Hz, enol); 3.90 (t, J = 7.1 Hz, 2H); 6.15 (q, J = 2.7 Hz, 2H), 6.65 (q, J = 2.7 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 204.2 (C=O); 190.7 (C=*C*–OH); 120.2 (C$_\alpha$); 107.6 (C$_\beta$); 68.6 (*C*=C–OH); 49.3 (CH$_2$–N); 31.3, 30.3, 28.9, 27.8, 27.3, 26.4, 26.2, 22.6 [(CH$_2$)$_5$ and CH$_3$ (enol and diketone)].

6DBM: Same procedure as for **6ACAC** using 1,3-diphenyl-1,3-propanedione instead of 2,4-pentanedione. Yield = 9%. IR: 3066 $\nu(\mathrm{C_{sp^3}-H})$; 2932 and 2864 $\nu(\mathrm{C_{sp^3}-H})$; 1687 cm^{-1}: $\nu(\mathrm{C{=}O})$. ^{1}H NMR (CDCl$_3$): δ 1.10–1.20 (m, 8H); 3.85 (t, J = 7.0 Hz, 2H); 5.2 (t, J = 6.6 Hz, enol); 6.15 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.0 Hz, 2H); 7.30–8.10 (m, 10H). ^{13}C NMR (CDCl$_3$): δ 198.6 (C=C–*C*=O); 136.0 (C=*C*–OH); 131.4 (C$_6$H$_5$); 130.0 (C$_6$H$_5$); 122.9 (C$_\alpha$); 110.3 (C$_\beta$); 68.6 (C=*C*–OH); 52.0 (CH$_2$–N) ; 33.9, 31.9, 31.7, 30.6, 28.9 [(CH$_2$)$_5$].

7-(Pyrrol-1-yl)heptanenitrile (6a) and 11-(pyrrol-1-yl)-undecanenitrile (6b). 6a: Sodium cyanide (1.080 mol) was partially dissolved in 250 mL of DMSO[21,22] and the solution heated to 80 °C. **5a** was slowly added under vigorous mechanical stirring for 10–15 min. The temperature then increased rapidly and remained between 135–145 °C. Once all of the **5a** had been added, the temperature quickly dropped and below 50 °C reaction was complete. The brown crude product was cooled, poured into water and extracted with diethyl ether. The yellow organic phase was washed several times with a saturated aqueous solution of sodium sulfate and dried over calcium chloride. The crude oil was purified by chromatography on silica gel with a solution of 5% diethyl ether–95% petroleum ether as eluent. Yield = 68–73%. IR: 3110 $\nu(\mathrm{C_{sp^2}-H})$; 2931 $\nu(\mathrm{C_{sp^3}-H})$; 2246 cm^{-1} $\nu(\mathrm{C{\equiv}N})$. ^{1}H NMR (CDCl$_3$): δ 1.30–1.85, (m, 8H); 2.35 (t, J = 6.8 Hz, 2H); 3.90 (t, J = 7.0 Hz, 2H); 6.10 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H).

6b: Some procedure as for **6a** using *N*-(10-bromodecyl) pyrrole instead of *N*-(6-bromohexyl)pyrrole. IR: 3105 $\nu(\mathrm{C_{sp^2}-H})$; 2925 and 2820 $\nu(\mathrm{C_{sp^3}-H})$; 2245 cm^{-1} $\nu(\mathrm{C{\equiv}N})$. ^{1}H NMR (CDCl$_3$): δ 1.30–1.85 (m, 16H); 2.35 (t, J = 6.9 Hz, 2H); 3.90 (t, J = 7.1 Hz, 2H); 6.10 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H).

3-(Pyrrol-1-yl)propanoic acid (2CA), 7-(pyrrol-1-yl)heptanoic acid (6CA) and 11-(pyrrol-1-yl)undecanoic acid (10CA). 2CA, **6CA** and **10CA**, were synthesized according to the procedure described in the literature[23] for **2CA**.

6CA: **6a** (1.200 mol) and 350 mL of a solution of potassium hydroxide (6.7 M) were refluxed until the organic phase disappeared (5–10 h). Water (100 mL) was added and the solution was acidified to pH 5 with hydrochloric acid (8 M). The crude product was extracted five times with diethyl ether, which was removed under reduced pressure to give a beige powder. Recrystallization was driven in hot *n*-heptane. Yield = 50–55%, m.p. = 60–61 °C. IR: 3100–2500 $\nu(\mathrm{O-H})$; 2860 $\nu(\mathrm{C_{sp^3}-H})$; 1700 cm^{-1} $\nu(\mathrm{C{=}O})$. ^{1}H NMR (CDCl$_3$): δ 1.10–1.90 (m, 8H); 2.35 (t, J = 7.3 Hz, 2H); 3.90 (t, J = 7.1 Hz, 2H); 6.15 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 179.6 (COOH); 120.3 (C$_\alpha$); 107.7 (C$_\beta$); 49.3 (CH$_2$–N); 33.7 (*C*H$_2$–COOH); 31.2, 28.4, 26.3, 24.3 [(CH$_2$)$_4$].

2CA: Same procedure as for **6CA** using 3-(pyrrol-1-yl) propanenitrile (commercially available) instead of 7-(pyrrol-1-yl)heptanenitrile. m.p. = 57–59 °C. IR: 3200–2400 $\nu(\mathrm{O-H})$; 2940 $\nu(\mathrm{C_{sp^3}-H})$; 1701 cm^{-1} $\nu(\mathrm{C{=}O})$. ^{1}H NMR (CDCl$_3$): δ 2.35 (t, J = 6.9 Hz, 2H); 4.20 (t, J = 6.9 Hz, 2H); 6.15 (t, J = 2.1 Hz, 2H); 6.70 (t, J = 2.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 177.3 (COOH); 120.4 (C$_\alpha$); 108.5 (C$_\beta$); 44.3 (CH$_2$–N); 36.2 (*C*H$_2$–COOH).

10CA: Same procedure as for **6CA** using 11-(pyrrol-1-yl) undecanenitrile instead of 7-(pyrrol-1-yl)heptanenitrile. m.p. = 66–68 °C. IR: 2500–3000 $\nu(\mathrm{O-H})$; 2910 $\nu(\mathrm{C_{sp^3}-H})$; 1691 cm^{-1} $\nu(\mathrm{C{=}O})$. ^{1}H NMR (CDCl$_3$): δ 1.20–1.45 (m, 12H); 1.50–1.90 (m, 4H); 2.35 (t, J = 7.2 Hz, 2H); 3.85 (t, J = 7.2 Hz, 2H); 6.15 (t, J = 2.1 Hz, 2H); 6.65 (t, J = 2.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 180.1 (COOH); 120.3 (C$_\alpha$); 107.6 (C$_\beta$); 49.5 (CH$_2$–N); 33.9 (*C*H$_2$–COOH); 31.4, 29, 26.6, 24.5 [(CH$_2$)$_8$].

Electrochemical set-up

Analytical experiments were performed in a three-compartment cell fitted with a saturated calomel reference electrode (SCE), a platinum electrode (diameter 2 mm) and a platinum counter electrode. The electrochemical apparatus was a Tacussel PGP 201 potentiostat (equipped with an integrated pilot for low to moderate scan rates), a Tacussel IG5-N integrator and a Sefram 164 plotter. The solvent was spectroscopic grade acetonitrile, distilled over phosphoric anhydride (to remove any trace of water or amines that may act as polymerization scavengers). Tetraethylammonium perchlorate (TEAP, Fluka, puriss, recrystallized once in acetonitrile–diethyl ether), or lithium perchlorate (Fluka, puriss) was added as the supporting electrolyte salt. The concentration of the monomers was usually between 5×10^{-3} and 10^{-2} mol L^{-1}.

For film studies, two cells were used in parallel, one containing a monomer solution for the film synthesis and another containing a clean electrolyte solution, where the films were transferred for electrochemical studies. The electrode was carefully cleaned with acetonitrile between each experiment. All films were prepared potentiostatically at 1.08 V (*vs.* SCE) by passage of a constant charge of 0.13 C cm^{-2} through an acetonitrile solution with either $LiClO_4$ or TEAP added (the electrolyte salt used for electropolymerization is indicated in brackets in the text or captions). Cycling of the films was performed in acetonitrile with either $LiClO_4$ or TEAP added (see text or captions) at a scan rate of 50 mV s^{-1}.

To study the influence of transition metal ions, a film was electrogenerated in acetonitrile solution containing 0.1 mol L^{-1} electrolyte salt (Et_4NClO_4 or $LiClO_4$). Then, CV was carried out in a monomer-free solution with the same electrolyte as used for the formation of the film. When a stable CV (*i.e.* first scan in Fig. 2) had been obtained (to eliminate possible memory effects in the polymer), the ACAC or DBM group functionalized films were immersed or not in triethylamine, rinsed with acetonitrile and finally cycled into acetonitrile containing 0.1 mol L^{-1} transition metal perchlorate as the supporting electrolyte.

Results and discussion

All the functionalized monomers readily polymerize in acetonitrile, although the formation of a polymer film at a usual rate requires a concentration of *ca.* 5×10^{-3}–10^{-2} mol L^{-1}, in the range of what is commonly used for classical electrochemical polythiophene synthesis[24] (while polypyrrole can be electropolymerized at lower concentrations[1,6]). Typical voltammograms are represented in Fig. 1. Doping levels (determined from the integration of cyclic voltammograms) are displayed in Table 1, these are usually in the 10–15% range, which is quite low when compared to polypyrrole[7] but is not too surprising for an N-functionalized pyrrole.[1]

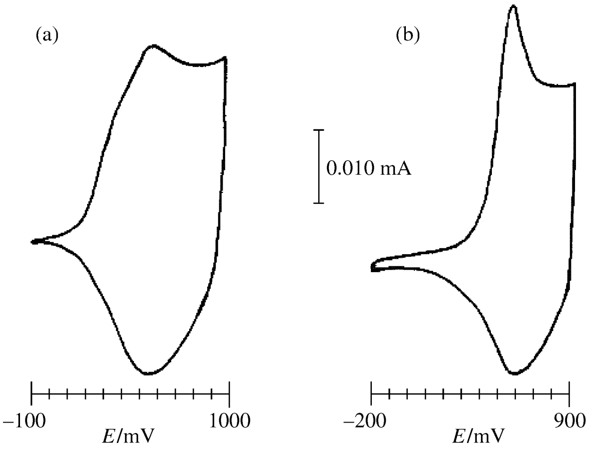

Fig. 1 Cyclic voltammetry of films of (a) poly(**6CA**) and (b) poly(**6DBM**) on a platinum electrode (diameter 2 mm) in 0.1 mol L^{-1} $LiClO_4$–CH_3CN.

Table 1 Oxidation potential values (E_{ox}) for each monomer. Oxidation and reduction peak potential (E_{p_a}, E_{p_c}) values of the corresponding homopolymers and their doping level δ

	Monomer	Polymer			
	E_{ox}/mV	E_{p_a}/mV	E_{p_c}/mV	ΔE_p/mV	δ^a
2CA	1380	655	530	125	0.142
6CA	1210	595	555	40	0.136
10CA	1255	595	530	65	0.153
6ACAC	1095	580	535	45	0.150
6DBM	1220	590	570	20	0.108

[a] $\delta = 2Q_d/(\rho Q_t - Q_d)$ with Q_d the doping charge (deduced from integration of the anodic zone of the voltammogram), Q_t the total charge of the electrolysis and ρ the electropolymerization efficiency (hypothesis: $\rho = 1$).

Behavior of the diketone functionalized pyrroles

The complexation power of the diketone functionalized pyrroles was evaluated by an UV-vis spectrophotometric study (Table 2). First, spectra were recorded for each compound used for this study [*i.e.* $M(ClO_4)_2$ where M represents Co(II) or Ni(II), diketone functionalized pyrroles (**6ACAC**, **6DBM**) and triethylamine (Et_3N) in acetonitrile (0.1 M)]. Then spectra of mixtures composed of $M(ClO_4)_2$ and β-diketone functionalized pyrrole with or without Et_3N in acetonitrile were obtained. The important absorption band shift of the metal ion indicating the reaction of cobalt(II) or nickel(II) with the pyrrolic derivative was observed only when Et_3N was added (see Table 2). It does not result from an interaction between Et_3N and Co(II) or Ni(II) since the spectra of a mixture of Et_3N and $M(ClO_4)_2$ in acetonitrile displays only a weak shift of the absorption band of the metal ion towards shorter wavelength (*i.e.* in the opposite direction). Furthermore, the similarities of the spectra obtained for the mixture of $Co(ClO_4)_2$, **6ACAC**, Et_3N and for Co(**6ACAC**)$_2$[25] confirm the reaction of Co(II) with **6ACAC**. When no base is added, only simple complexation with ACAC occurs and this does not affect the UV-vis spectrum of the metal.

The behavior of the DBM functionalized films is quite similar to that of classical N-substituted polypyrroles.[26,27] However, its electrochemical behavior is only slightly or not at all modified when changing the electrolyte salt, even when the electrolyte is a transition metal salt. This is in contrast to

Table 2 UV-vis spectrophotometric study of Co(II) and Ni(II) complexation by **6ACAC**

System[a]	Co(II)[b]	Ni(II)[b]
$M(ClO_4)_2$	490(0.126)	368(0.061) 595(0.039)
$M(ClO_4)_2$ + Et_3N	469(0.180) 631(0.050)	Precipitates
$M(ClO_4)_2$ + **6ACAC**	488(0.154)[c]	595(0.040)[c]
$M(ClO_4)_2$ + **6ACAC** + Et_3N	446 sh[c] 580(0.170) 635(0.174)	666(0.044)[c]
M(**6ACAC**)$_2$	589(0.608)[c] 685(0.675)	

[a] Concentration of each compound: 0.1 mol L^{-1} in acetonitrile. [b] Data are given in the form wavelength/nm (intensity). [c] β-Diketone functionalized pyrroles absorbed strongly at $\lambda \approx 315$ nm (intensity ≈ 3).

the classical behavior of functionalized polypyrroles, which are generally sensitive to a modification of the substituted moieties, as exemplified by the case of biosensors.[28] Although the UV-vis study shows the ability of **6DBM** to complex Ni and Co ions, no change is observed in the case of poly(**6DBM**), maybe because of the restricted mobility of the DBM groups.

In contrast, the ACAC functionalized polypyrroles exhibit behavior that depends on the complexation of the functional group. An anodic peak shift is observed upon cycling in an electrolyte containing a transition metal such as Ni^{2+} or Co^{2+} (Fig. 2). Treatment with triethylamine (Et_3N), followed by cycling in a solution containing a transition metal ion results in the same qualitative effect, albeit to a lesser extent. There is no splitting of the polymer peak, but the large anodic shift clearly shows the structural change of the polymer. Upon cycling again in lithium perchlorate, the CV of the polymer first remains stable, then changes again, but does not return to the initial state; this is probably due to mechanical changes in the film due to the high level of incorporation of the transition metal ions.[29]

This has been confirmed by an IR study of the films under different conditions, upon comparing the frequencies and the relative intensities of the carbonyl and perchlorate bands in the polymers. Table 3 summarizes the IR data on the polymers, according to the electrochemical treatment to which they were submitted (just after synthesis, after cycling in a transition metal solution and finally, first cycled in $Ni(ClO_4)_2$ and then cycled again in $LiClO_4$). First of all, the frequency of the ACAC carbonyl stretching band is decreased by 10–15 cm^{-1}, compared to the monomer. This results from complexation by the electrolyte cations. This is confirmed by the analysis of the relative intensities of the bands. Immediately after synthesis in $LiClO_4$, the ratio $R = I[\nu(C{=}O)]/I[\nu(ClO)] = 0.81$, the perchlorate present acting as the doping species of the polymer; there is probably close to one perchlorate for 7 to 10 pyrrole rings. Upon cycling in $Co(ClO_4)_2$ or $Ni(ClO_4)_2$ this ratio decreases to 0.12 or 0.16, respectively, indicating thus a large increase of the amount of perchlorate in the film. Moreover, a quantitative analysis of the above figures shows that, relying on 0.1–0.15 perchlorates per pyrrole ring in the as-grown state (as determined from the coulometric data), the amount of perchlorate in the films cycled with transition metal ions is now close to 6–7 times more, that is close to 1 perchlorate per pyrrole ring. This shows not only that the complexation is nearly quantitative, but also that simple complexation of the metal ions takes place on the ACAC, without exchange of the labile ACAC protons.[25] Upon cycling (3 cycles) the films again in $LiClO_4$, R increases again to 0.31, indicating a decrease in the amount of perchlorate, associated with the slow incomplete release of the transition metal. In the case of the DBM modified film, on the other hand, no significant change was found between the different spectra, as could be expected. All these measurements confirm, and allow us to quantify, the previously discussed electrochemical results.

However, we did not observe any reduction of the transition metal inserted in the film. This behavior is in accordance with the results of Richter and Bard from electrochemical studies of europium diketonates.[30] In our case, this may also result from the non-conductive character of the film at highly reducing potentials, which suppresses connections between the redox centers and the electrode.

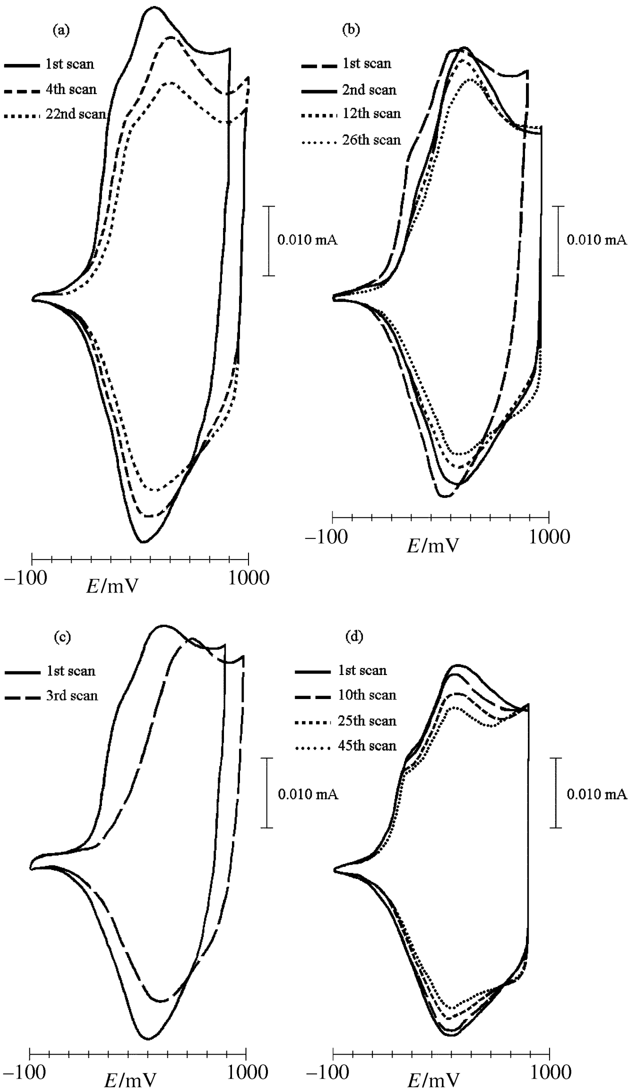

Fig. 2 Cyclic voltammetry of poly(**6ACAC**) film in 0.1 mol L^{-1} $LiClO_4$–CH_3CN (first scan) then (for the other scans) in (a) 0.1 mol L^{-1} $Ni(ClO_4)_2$–CH_3CN, (b) 0.1 mol L^{-1} $Ni(ClO_4)_2$–CH_3CN after immersion in Et_3N, (c) 0.1 mol L^{-1} $Co(ClO_4)_2$–CH_3CN after immersion in Et_3N, (d) 0.1 mol L^{-1} $LiClO_4$–CH_3CN. [$LiClO_4$].

Behavior of the carboxylic group functionalized polymers (CA polypyrroles)

CA polypyrroles exhibit a quite different behavior depending on the electrolyte medium. Newly electropolymerized films of

Table 3 Effect of the metal ion from the electrolytic solution on the IR data of poly(**6ACAC**) films, after cycling in several acetonitrile solutions containing 0.1 mol L^{-1} of the metal salts

		As grown (in $LiClO_4$)	Cycled in $Co(ClO_4)_2$	Cycled in $Ni(ClO_4)_2$	Re-cycled in $LiClO_4$ after cycling in $Ni(ClO_4)_2$
C=O	ν_1/cm^{-1}	1699	1697	1698	1700
	I_1	18.5	6.4	8.3	14.4
Cl–O	ν_2/cm^{-1}	1085	1085	1084	1084
	I_2	22.8	53.2	52.0	46.6
$R = I_1/I_2$		0.81	0.12	0.16	0.31

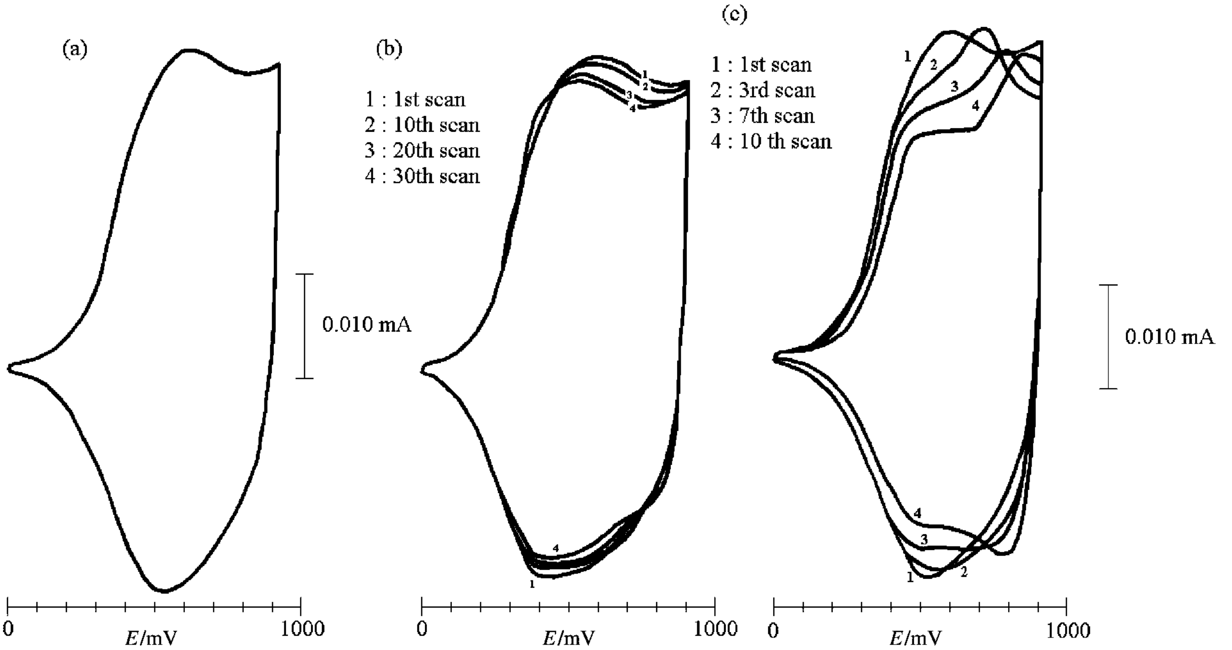

Fig. 3 Cyclic voltammetry of poly(**6CA**) films in the presence of Li^+ ions: (a) first scan in 0.1 mol L^{-1} TEAP–CH_3CN, (b) successive scans in 0.1 mol L^{-1} $LiClO_4$–0.1 mol L^{-1} $HClO_4$–CH_3CN; (c) successive scans in 0.1 mol L^{-1} $LiClO_4$–CH_3CN. [TEAP].

poly(**6CA**) [Fig. 3(a)] are certainly in the acidic state due to the excess of protons produced by the electropolymerization reaction in the vicinity of the carboxylic groups. When the films are cycled in an acidic electrolyte (with 0.1 mol L^{-1} perchloric acid added) very stable CVs are obtained as shown in Fig. 3(b), very similar to the initial CV. However, when neutral acetonitrile is used as the electrolyte, the CV progressively changes as a result of the deprotonation of the carboxylic acid and exchange with the electrolyte cations. This process is especially favored when Li^+ is the electrolyte cation, which is not unexpected given the acidity of this cation in acetonitrile. This is attested to by the splitting of the initial polymer peak and its progressive replacement by another redox couple at a higher potential [*ca.* 200 mV, see Fig. 3(c)].

This has again been confirmed by an IR study, by comparing the relative intensities of the carbonyl and the perchlorate bands. The frequencies and relative intensities of the bands are displayed in Table 4, similarly as in Table 3, for as-grown films of poly(**6CA**) (in TEAP), films cycled in $LiClO_4$–$HClO_4$ and films cycled with $LiClO_4$ without added acid. In as-grown films in TEAP, the ratio R is 2.0. This ratio comes down to 0.70 when the polymer is cycled in the presence of perchloric acid, and comes up again to 3.3 when the polymer is cycled in pure $LiClO_4$. It can be assumed that in the presence of perchloric acid the carboxylic groups in the polymer are totally protonated, therefore excluding any self-doping by the carboxylate; the low ratio found is due to the large amount of perchlorate anions in the polymer (typically one for four pyrrole rings, according to ref. 7). In the other situations, and especially when the film is cycled in the presence of $LiClO_4$, some of the carboxylic groups are deprotonated and the resulting carboxylates participate in the doping process (self-doping).[31] The high ratio in the third case shows that the polymer, upon cycling in pure $LiClO_4$, is almost exclusively self-doped.

Table 4 Effect of the metal ion from the electrolytic solution on the IR data of poly(**6CA**) films, after cycling in several acetonitrile solutions containing 0.1 mol L^{-1} each of the electrolyte salts

		TEAP	$LiClO_4$ + $HClO_4$	$LiClO_4$
C=O	ν_1/cm^{-1}	1706	1708	1707
	I_1	36.4	31.2	37.7
Cl–O	ν_2/cm^{-1}	1080	1083	1083
	I_2	18.1	44.8	11.4
$R = I_1/I_2$		2.01	0.70	3.31

It should be noted that the frequency of the C=O band was almost constant in the three cases examined, which seems contradictory to the preceding interpretation, because the self-doped polymer should display the C=O carboxylate band, which is usually situated *ca.* 100 cm^{-1} lower than the corresponding carboxylic acid.[32] This can be explained by the fact, that, in the case of the self-doped polymer, approximately 90% of the carboxylic groups are still in the acidic form, because the doping level is only about 10% (see Table 1) and therefore only 10% of carboxylate groups participate in the self-doping process. Their contribution to the IR spectra is masked by the broad carboxylic acid band. The determination of the amount of perchlorate in the film is therefore, although indirect, a much better indicator of the dopant nature.

The electrochemical behavior observed for the CA polypyrrole films is largely independent of the length of the link between the pyrrole and the carboxylic group, since poly(**10CA**) and poly(**2CA**) display analogous behavior (Fig. 4) to that of poly(**6CA**). Nevertheless, the effect on poly(**2CA**) is less striking. As the alkyl chain of **2CA** (2 CH_2) is shorter, the approach of the Li^+ cation is probably disturbed by electrostatic repulsion between the charge carrier (polaron or bipolaron) in the oxidized polymer chain and the positive charge of the Li^+ cation. In the case of poly(**6CA**) and poly(**10CA**) electrostatic repulsions are likely to be much weaker because of the longer alkyl chains of **6CA** (6 CH_2) and **10CA** (10 CH_2) and consequently deprotonation by Li^+ would be more efficient.

The behavior of the CA polypyrroles has also been studied in water. Under such conditions, only poly(**2CA**) has been found to display a significant electroactivity, since in the case of the higher homologs, the larger hydrophobicity of the chain impedes the presence of enough water in the polymer [as attested by the flat cyclic voltammograms obtained after 3–4 cycles with poly(**6CA**) and poly(**10CA**)]. The electrochemical response of poly(**2CA**) is shown on Fig. 5 at different pH. It is clear that both the shape of the voltammograms and the peak potentials change with pH, but, even in the case of the well-

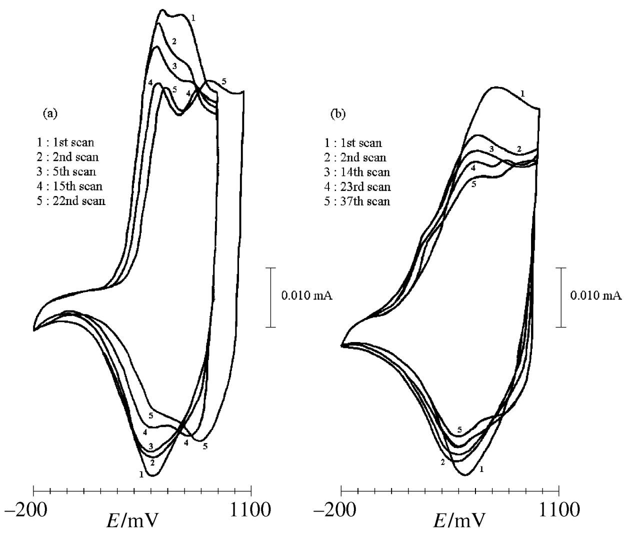

Fig. 4 Cyclic voltammetry in 0.1 mol L^{-1} TEAP–CH_3CN (first scan) then in 0.1 mol L^{-1} $LiClO_4$–CH_3CN (following scans) of (a) poly(**10CA**) and (b) poly(**2CA**) films. [TEAP].

defined reduction peak, the dependence of the peak potential *vs.* pH is not linear, indicating a complex behavior.

Cycling the CA polypyrroles in an electrolyte containing transition metal ions also affects the behavior of the films, as shown by Fig. 6. It is worth noting that with CA polypyrroles, especially in the case of Co^{2+} cations, the shift of the anodic peak occurs in the direction of more negative (lower) potentials in contrast to what is observed with poly(**6ACAC**).

Copolymers

The copolymerization of all monomers with pyrrole (Py) is feasible and results in a random copolymer, the redox potential of which varies with the composition of the films. Fig. 7 displays the calculated potential $E°$ shift variation *vs.* x, the relative proportion of the functionalized pyrroles (fPy) in the polymerization feed:

$$E° = \frac{E_{\mathrm{Pa}} + E_{\mathrm{Pc}}}{2} \quad \text{and} \quad x = \frac{n_{\mathrm{fPy}}}{n_{\mathrm{Py}} + n_{\mathrm{fPy}}}$$

It is clear that a similar trend is followed in all cases, the peak potentials increasing with the proportion of functionalized pyrroles in the synthetic feed, which in turn should be related to the proportion of functionalized species in the final electrogenerated polymer. This shows clearly that there is a modification of the polymer.

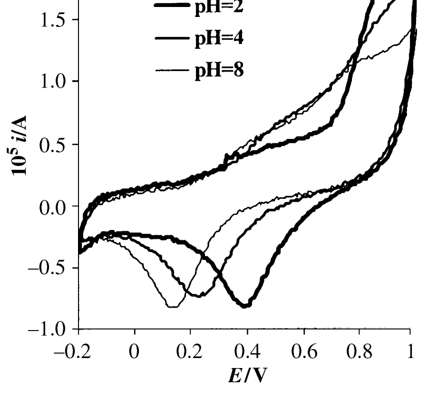

Fig. 5 Cyclic voltammetry of poly(**2CA**) films in 0.1 mol L^{-1} $LiClO_4$–H_2O at pH 2, 4 and 8.

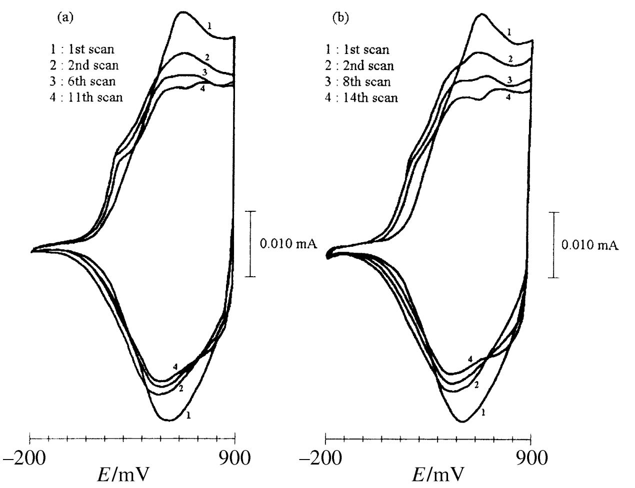

Fig. 6 Cyclic voltammetry of poly(**6CA**) films in the presence of Ni^{2+} or Co^{2+} ions: first scan in 0.1 mol L^{-1} TEAP–CH_3CN and following scans in (a) 0.1 mol L^{-1} $Ni(ClO_4)_2$–CH_3CN, (b) 0.1 mol L^{-1} $Co(ClO_4)_2$–CH_3CN. [TEAP].

However, CA pyrroles and β-diketone pyrroles display different behavior as a function of x. The potential $E°$ increases only when x is greater than 0.5 and 0.75 for **6ACAC** and **6DBM**, respectively [Fig. 7(a)]. At lower x values $E°$(copolymer) is very close to $E°$(polypyrrole); it is clear that only polypyrrole is made as long as the functionalized

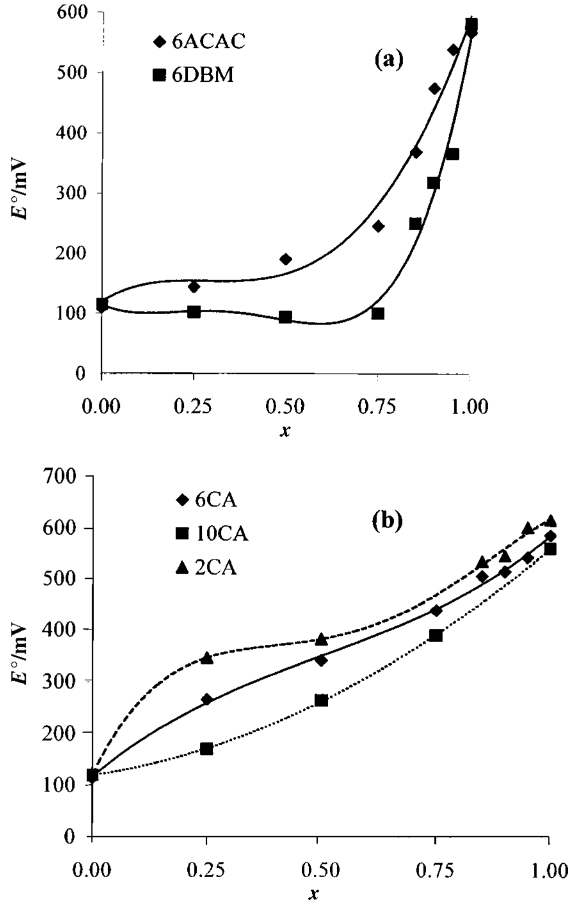

Fig. 7 Electrochemical copolymerization of pyrrole (Py) and functionalized pyrrole (fPy): $E°$ *vs.* relative proportion x of (a) **6ACAC** and **6DBM**; (b) **6CA**, **10CA** and **2CA** in the polymerization feed. Electrochemical synthesis of each film was performed at 1080 mV by passing 0.13 C cm^{-2} through a mixture of pyrrole and functionalized pyrrole ([Py] + [fPy] = 10^{-2} mol L^{-1}) in 0.1 mol L^{-1} $LiClO_4$–CH_3CN.

monomer is not in excess relative to unsubstituted pyrrole in the feed. The difficulty of obtaining a copolymer may be due to the steric hindrance of the β-diketone group; indeed, for the DBM (bulkier than ACAC) moiety, the synthetic feed must be more concentrated in **6DBM** to obtain a copolymer.

As shown Fig. 7(b), $E°$(copolymer) > $E°$(polypyrrole) for all x values; the copolymerization of CA pyrrole with pyrrole seems to be easier. For each value of x, $E°$[poly(**2CA**)] > $E°$[poly(**6CA**)] > $E°$[poly(**10CA**)]; when the alkyl chain is shorter, $E°$ is higher. But for $x < 0.6$, the difference in $E°$ between copolymers obtained at a given value of x is greater than when $x > 0.6$. From this observation we deduce that, for a given x, the copolymer film is richer in **2CA** and poorer in **10CA**. A plausible explanation lies in the influence of the length of the alkyl chain during the electropolymerization; **2CA**, which possesses the shortest alkyl chain of the CA series has lower steric hindrance than **10CA** with the longest alkyl chain. The weak steric hindrance of **2CA** does not prevent its insertion in the growing film even if the synthetic feed is richer in pyrrole. Under the same conditions the bulkiness of **10CA** represents a handicap. **6CA** shows an intermediate behavior between **10CA** and **2CA**. It should be noted that the contrary would have been expected if one considered only the relative order of the oxidation potentials of pyrrole and the CA pyrroles.[33]

However, it is not obvious from this data how the proportion of the functionalized moieties in the film depends on the relative amount of the monomers in the feed. An IR spectroscopic study allows us to confirm the electrochemical observations. The calculated ratio $R = I_1/I_3$ where I_1 represents the carbonyl peak intensity [characteristic of CA (at *ca.* 1700 cm^{-1}), ACAC (at 1710 cm^{-1}) and DBM (at 1685 cm^{-1}) pyrroles] and I_3 the pyrrolic ring stretch (at 1540 cm^{-1}) intensity, increased with the proportion of functionalized monomers in the synthetic feed. Moreover, the proportion (p) of the functionalized pyrrole moieties in the copolymer can be estimated by the following relation:

$$p = \frac{I_1(x) \times I_3(x = 1)}{I_1(x = 1) \times I_3(x)}$$

The proportion (p) of functionalized pyrrole in the film (Fig. 8), estimated through this method, is again smaller than the one in the synthetic feed as previous studies on pyrrole copolymers tend to show.[34,35] These results are very reminiscent of the conclusions of the aforementioned electrochemical study. This is certainly due to the higher polymerizability of pyrrole, and can only be ascertained by elemental analysis. However, in our case this technique would only give poorly reliable results, due to the very similar compositions of both monomers.

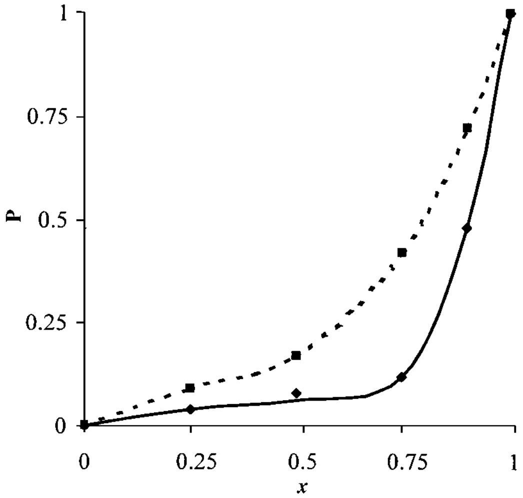

Fig. 8 IR spectroscopic study of the copolymers. Composition of the copolymer films in functionalized pyrrole *vs.* x, the relative proportion of **6CA** (dashed line) and **6ACAC** (solid line) in the polymerization feed. Electrochemical conditions as for Fig. 7.

Conclusion

We have prepared and polymerized several pyrroles functionalized with cation complexing or anchoring functions. Although the electrochemical study as well as the IR data demonstrate that complexation occurs with transition metal ions, the efficiency of the process remains average and sensitivity must be improved for use in the sensor field. The copolymer synthesis appears to occur analogously to previously reported examples,[34,35] with incorporation of the functionalities in the copolymer being related to the proportion of functionalized pyrrole in the feed. In addition, Armes and co-workers used analogous molecules for the preparation of polypyrrole silica colloidal nanocomposites.[23] We have therefore turned our attention towards the electrochemical preparation of polypyrrole–oxide composites using our functionalized pyrroles.

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