

Electroreductive polymerisation of 3-substituted 2,5-dihalothiophenes: direct electrosynthesis *vs.* stepwise procedure involving thienylzinc intermediates

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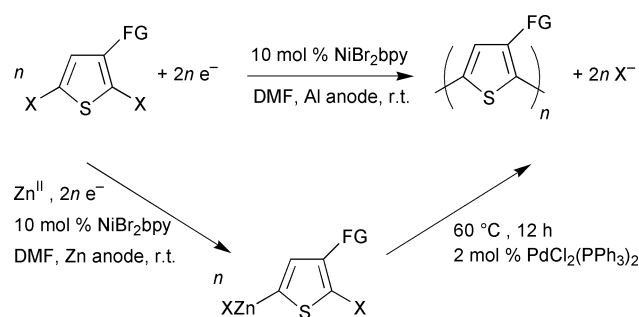
This work deals with the preparation of 3-substituted polythiophenes from the corresponding 3-substituted 2,5-dihalothiophenes, either in one electrochemical step or in two steps involving electrogenerated thienylzinc intermediates. The mild conditions used all along these electrochemical procedures allow the preparation of polythiophenes functionalised by a variety of groups in the 3 position. Poly(3-hexylthiophene) prepared in two steps shows a high proportion of regioregular HT-HT linkages (HT = head-to-tail). Most polymers exhibit p-doping processes in cyclic voltammetry. n-Doping processes are also observed for polythiophenes substituted either by alkyl groups or by electron-withdrawing groups.

Recent developments in the preparation of 3-substituted polythiophenes have focused on control of the conjugation length in order to improve the electronic properties of these materials.¹ In this context, several synthetic routes, based on the regioselective activation of the 5 position of the thiophene ring, have been found to provide access to regioregular 3-substituted polythiophenes. The corresponding procedures involve the preparation of thienylmagnesium^{2–6} (Mc Cullough method), thienylzinc^{7–11} (Rieke's method) or thienylborane (Bidan's method)¹² intermediates, which undergo polymerisation under appropriate coupling conditions. Regioregular poly(3-alkylthiophenes) have been prepared by these methods.

In addition, these organometallic polymerisation procedures appear to be less dependent on the electronic effects of the groups in the 3 position than the classical direct electro-oxidation of the corresponding monomers. Indeed, poly(3-thioalkylthiophenes) have been prepared by Rieke *et al.*¹⁰ Yamamoto *et al.* used stoichiometric amounts of zerovalent nickel complexes to carry out the polymerisation of 3-carbonitrilethiophene.¹³ Polythiophenes substituted by such electron-donating and -withdrawing groups, respectively, are hardly accessible by electro-oxidation methods.¹⁴ However, the use of strong organometallic reagents precludes the presence of sensitive groups in the 3 position, and the above-mentioned procedures have only been applied to the preparation of polythiophenes substituted by alkyl, thioalkyl or aryl groups.

This work deals with the electrochemical preparation of polythiophenes substituted by a variety of groups in the 3 position. Polymerisation is performed from the corresponding 3-substituted 2,5-dihalothiophenes either in one nickel-catalysed electroreductive step, or through the intermediate electrosynthesis of thienylzinc species, which subsequently undergo palladium-catalysed coupling under Negishi conditions. Both pathways are represented in Scheme 1.

The preparation of the monomers has already been reported,¹⁵ namely the electrochemical functionalisation of thiophene in the 3 position by benzyl, aryl, or activated aliphatic groups, the bromination of both 2 and 5 positions and the consecutive nickel-catalysed electrochemical conversion to



Scheme 1

thienylzinc species. The structural and redox properties of the resulting polymers are discussed in this work.

Experimental

Reagents

The *N,N*-dimethylformamide (DMF) used as solvent was purchased from SDS (analytical grade) and used without further purification. Acetonitrile (extra dry; water <10 ppm) was purchased from Acros and used without further purification. The functionalisation, bromination, and electrochemical activation by zinc of thiophene monomers is fully described in ref. 15. Tetrabutylammonium tetrafluoroborate was purchased from Fluka and recrystallised in diethyl ether. The NiBr_2bpy ($\text{bpy} = 2,2'$ -bipyridine) catalyst precursor was prepared in absolute ethanol from stoichiometric amounts of NiBr_2 and 2,2'-bipyridine (typically 50 mmol in 250 cm³ ethanol), stirred overnight, filtered and dried under vacuum for 12 h. $\text{PdCl}_2(\text{PPh}_3)_2$ catalyst was purchased from Aldrich.

Protocol of reactions

One-step electrochemical polymerisation of 3-substituted 2,5-dihalothiophenes was carried out in 50 cm³ from 5 mmol of

thiophene monomer and 0.5 mmol of NiBr₂bpy catalyst (10 mol %) at a constant current of 0.1 A in an undivided cell fitted with a nickel foam cathode and a sacrificial aluminium anode. The cathode potential was monitored *vs.* a saturated calomel electrode (SCE) all along the electrolysis.

The electrochemical preparation of thienylzinc species was achieved from 5 mmol of original 3-substituted 2,5-dihalo-thiophenes and has already been described in ref. 15. The Pd-catalysed Negishi polymerisation of the resulting thienylzinc species was carried out in the same medium (DMF) by adding 140 mg of PdCl₂(PPh₃)₂ (0.2 mmol). The solution was stirred and heated (60 °C) for 12 h.

After the one- or two-step polymerisations, the DMF solutions were poured into aqueous 6 N HCl solutions (0.1 N HCl for thiophenes substituted by an ester group, in order to prevent hydrolysis of the ester). The resulting precipitate was filtered and washed with the same solution, then several times with distilled water, methanol and pentane in order to remove low-mass oligomers. For poly(3-alkylthiophenes), the solid residue was purified on a Soxhlet extractor with the same solutions. Finally, the polymers were dissolved in chloroform, re-precipitated in methanol, and dried under vacuum for 12 h. Polythiophenes substituted by ester or acetyl groups were not recovered as powders, but as oily materials partially soluble in most solvents. These polymers were washed with pentane and methanol in order to remove oligomers and dried under vacuum.

Apparatus

Electrolyses were carried out using an HP E3611 A DC power supply at a constant current of 0.1 A in all experiments. Cyclic voltammograms were recorded using an EG&G-PARC 273A potentiostat and the M270 electrochemical software. The concentration of the non-polymeric substrates was monitored by GC using an internal standard (dodecane or tetradecane). IR spectra were recorded from KBr pellets on a Perkin Elmer 577 FTIR spectrophotometer. UV-Vis spectra were recorded on a Cary spectrophotometer. ¹H-NMR spectra were recorded in CDCl₃ on a Bruker AC 200 spectrometer. MALDI-TOF-MS spectra were realised at the Laboratoire de Chimie Structurale Organique et Biologique (LCSOB; Université Pierre et Marie Curie, Paris) using dithranol as matrix and either AgTFA or NaI as cationisation salts.

Polymer characterisation

Polymers that are not listed below could only be characterised through their redox properties.

Polythiophene. Brown powder insoluble in CHCl₃. IR (KBr, cm⁻¹): 1492; 1458 (δ C=C); 791 (ν C-H).

Poly(3-methylthiophene). Reddish-brown powder partially soluble in CHCl₃. SEC: M_n =1469, M_w =2047, polydispersity=1.39. UV-Vis: λ_{max} =412 nm. ¹H-NMR (CDCl₃, 200 MHz) δ : 7.33–6.86 (m, 1H); 2.34–1.89 (m, 3H).

Poly(3-hexylthiophene). Reddish-brown powder soluble in CHCl₃. UV-Vis: λ_{max} =413 and 364 nm. ¹H-NMR (CDCl₃, 200 MHz) δ : 6.95 (s, 1H); 2.92–2.63 (m, 2H); 1.76–1.62 (m, 2H); 1.42–1.15 (m, 6H); 1–0.78 (m, 3H).

Poly(thiophen-3-yl-acetic acid ethyl ester). Brown oil partially soluble in CHCl₃. ¹H-NMR (CDCl₃, 200 MHz) δ : 7.35–6.85 (m, 1H); 4.2–3.8 (m, 2H); 3.6–6.2 (m, 2H); 1.25–0.82 (m, 3H).

Poly(2-thiophen-3-yl-propionic acid methyl ester). Brown oil soluble in CHCl₃. UV-Vis: λ_{max} =366 nm. ¹H-NMR (CDCl₃,

200 MHz) δ : 7.4–6.95 (m, 1H); 4–3.8 (m, 1H); 3.6–3.2 (m, 3H); 1.25–1 (m, 3H).

Poly(3-cyanothiophene). Brown powder weakly soluble in CHCl₃. IR (KBr, cm⁻¹): 2240 (ν C \equiv N); 747, 495 (ν C–I). UV-Vis: λ_{max} =375 nm.

Poly(3-acetylthiophene). Brown-purple powder soluble in CHCl₃. ¹H-NMR (CDCl₃, 200 MHz) δ : 7.44–7.25 (m, 1H); 2.59–2.18 (m, 3H).

Results and discussion

One-step nickel-catalysed polymerisation of 3-substituted 2,5-dihalo-thiophenes

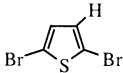

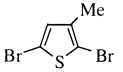

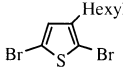

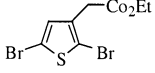

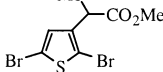

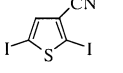

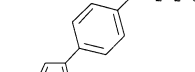

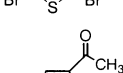

Electroreductive polymerisation of 3-substituted 2,5-dihalo-thiophenes was carried out in DMF, in an undivided cell fitted with an aluminium sacrificial anode, according to the overall reaction shown at the top of Scheme 1. The electrolysis was achieved at a constant current of 0.1 A until total consumption of the original 3-substituted 2,5-dihalo-thiophene; the charge passed followed the expected 2 Faraday per mole slope. 2,5-Dibromo-3-methylthiophene was first used as a test compound for the optimisation of the reaction. During the electrolysis, the DMF solution turned deep brown, while reddish-brown particles were formed within the solution. After the electrolysis, the cathode was covered by a thick brown deposit. The solid formed was extracted from both the solution and the cathode, and purified. The measurement of the molecular weight of the polymer by SEC gave a value of M_w =2047 Daltons. The mass of solid recovered gave a 46% isolated yield for poly(3-methylthiophene). This yield seems to be affected by the formation of soluble oligomers, as well as by the formation of a hydrogenated compound (2- and/or 5-bromo-3-methylthiophene), which is detected by GC during the electrolysis. The potential of the cathode shifts from –1.2 V/SCE at the beginning of the electrolysis (assigned to the reduction of the Ni^{II} catalyst) to –2 V/SCE as the polymer progressively deposits. The results obtained for various 3-substituted-2,5-dibromothiophenes are presented in Table 1.

The yields obtained by this one-step procedure are moderate. For most thiophenes, this can be explained by the formation of both soluble oligomers and α -hydrogenated thiophenes. Considering that these hydrogenated monomers could also be incorporated into the polymer backbone, they would cause chain termination as they only react on one side. Moreover, some polymers were partially soluble in most solvents, and therefore were difficult to isolate from their monomers. However, ¹H-NMR spectra recorded from the chloroform-soluble fraction of these polymers exhibit proton resonances related to the functional group in the 3 position of the thiophene ring, underlining the good functional compatibility of this one-step electrochemical process. This procedure also favourably compares with Yamamoto's method,¹³ since only catalytic amounts of nickel are required. The structural and redox properties of the polymers are discussed in the last paragraph of this section.

Polymerisation *via* intermediate thienylzinc species

We carried out the preparation of 3-substituted polythiophenes in two steps, through the electrochemical synthesis of intermediate thienylzinc species and their consecutive palladium-catalysed coupling, according to the pathway shown at the bottom of Scheme 1. The electrochemical preparation of thienylzinc species has already been reported.¹⁵ The palladium-catalysed coupling of these species is achieved in the same medium (DMF) at 60 °C for 12 h. The yields obtained by this

Table 1 Yields in one- and two-step polymerisation of 3-substituted 2,5-dihalo thiophenes

Monomer	Polymer	Isolated yields ^a (%)	
		One-step process	Two-step process
		33	40
		46	80
		45	60
		35	65
		35	50
		25	—
		—	30
		—	35

^a Yield calculated *vs.* original 2,5-dihalo thiophene based on the mass of solid recovered, neglecting the mass of possible halogen end-groups.

procedure are significantly higher for the same polymer than those reported from the one-step process, as seen in Table 1. As a matter of fact, polymers prepared in two steps show a more powdery aspect than their analogues from the one-step procedure. This could be ascribed to a higher degree of polymerisation, the polymers being therefore more selectively extracted. Moreover, by-products such as α -protonated monomers are formed in much lower amounts than in the one-step procedure, allowing longer chains. It must be pointed out that excess Zn^{II} is necessary for the palladium coupling to take place. Several experiments carried out without excess zinc salts led to the expected thienylzinc species, but they did not react even if excess Pd is used or the solution heated to 120 °C. We do not have a satisfactory interpretation of this behaviour, which requires a separate thorough study. However, a variety of 3-substituted polythiophenes are obtained by this process in only two steps and using mild conditions.

Structural characterisation of polythiophenes

We have studied the structural properties of polythiophenes prepared both in one and two steps by several techniques, including $^1\text{H-NMR}$, UV-vis spectrophotometry and MALDI-TOF-MS. These techniques allow the comparison of both synthetic procedures in terms of conjugation length and regioregularity of the resulting polymers. For this, we first focused on a well-described chloroform-soluble polythiophene, poly(3-hexylthiophene), since this particular material has been widely characterised by the groups of both McCullough³ and Rieke.⁷

Poly(3-hexylthiophene). The UV-visible spectra of poly(3-hexylthiophene) prepared in one or two steps are presented in Fig. 1. Poly(3-hexylthiophene) prepared in one step shows a broad spectrum above 300 nm. Its analogue prepared through the intermediate 2-bromo-5-bromozincio-3-hexylthiophene exhibits a much more defined spectrum, with two maxima at 364 and 413 nm. This difference may be ascribed to a higher conjugation length for the polymer prepared in two steps, together with a lower polydispersity.

The $^1\text{H-NMR}$ spectra of the chloroform-soluble fraction of both polymers are reported in Fig. 2. The “fingerprint” of the hexyl sidechain is present in both spectra in the alkyl region, but the spectra exhibit dramatic differences for the aromatic protons. Poly(3-hexylthiophene) prepared in one step shows a broad signal between 6.3 and 7 ppm, whereas a unique sharp peak is observed at 6.90 ppm for the same polymer prepared in two steps. This latter spectrum reveals the regioregularity of the polymer prepared in two steps, and its general shape is akin to the one reported for the same regioregular polymer by Rieke⁷ and McCullough.³

The MALDI-TOF-MS of poly(3-hexylthiophene) prepared in two steps is presented in Fig. 3. This spectrum exhibits successive peaks separated by 166 mass units, which corresponds to the mass of the monomer. The spectrum also shows peaks arising from $(166 + 1 + 1)$, $(166 + 80 + 1)$, and a few $(166 + 80 + 80)$ fragments that depend on the end-group atoms being hydrogenated on both end positions, hydrogenated on one side and brominated on the other, or brominated on both sides, respectively. Hydrogen end atoms may arise from hydrolysis of thienylzinc terminations, as mentioned by McCullough and Lowe for thienylmagnesium end-groups.² The highest intensity peaks are obtained for masses of *ca.* 4000, which corresponds to 24 monomer units.

These UV-vis, $^1\text{H-NMR}$ and MALDI-MS spectra show that poly(3-hexylthiophene) prepared in two steps is regioregular. Its analogue prepared in one step is not as well-defined. This polymer could be more dispersed when prepared in one step, it could also be regiorandom, or both. As a matter of fact, the recovery and passivation of the cathode may affect the chain growth in the one-step process. A polydispersed polythiophene would not give satisfactory structural data even if it has a regioregular structure.

Other 3-substituted polythiophenes. The structural differences depicted for poly(3-hexylthiophene) prepared in one or two step are observed with all 3-substituted polythiophenes. However, additional difficulty is met during the purification steps, since some polymers and their monomers or oligomers have very similar solubility properties in most organic

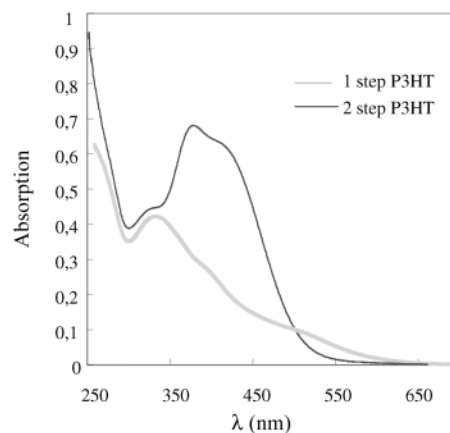


Fig. 1 UV-Vis spectra of poly(3-hexylthiophene) (P3HT) prepared in one or two steps.

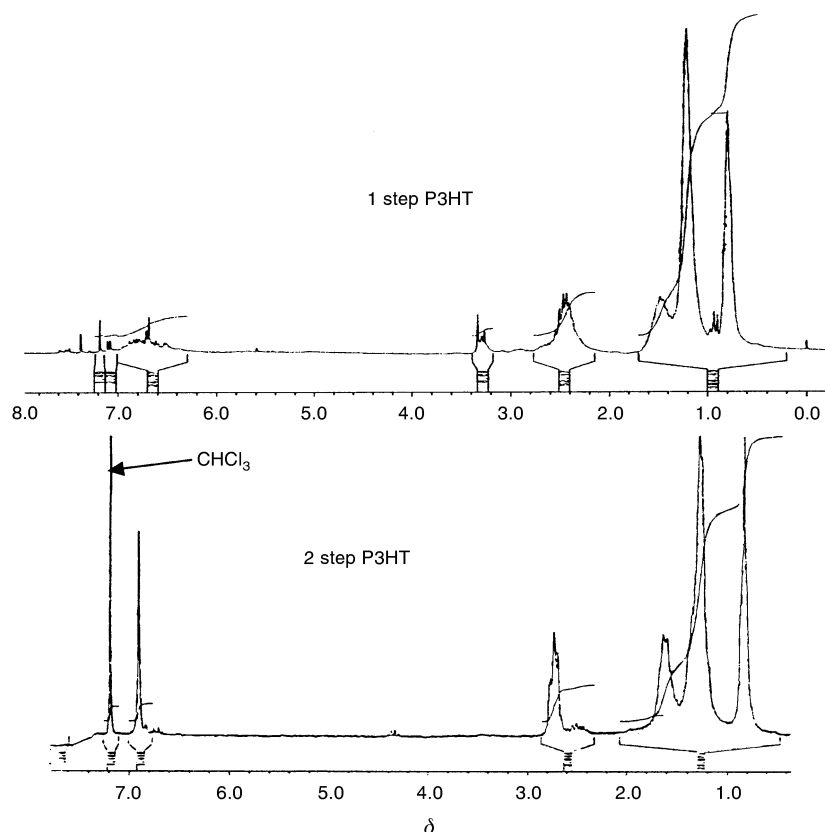


Fig. 2 ^1H -NMR spectra of P3HT prepared in one or two steps.

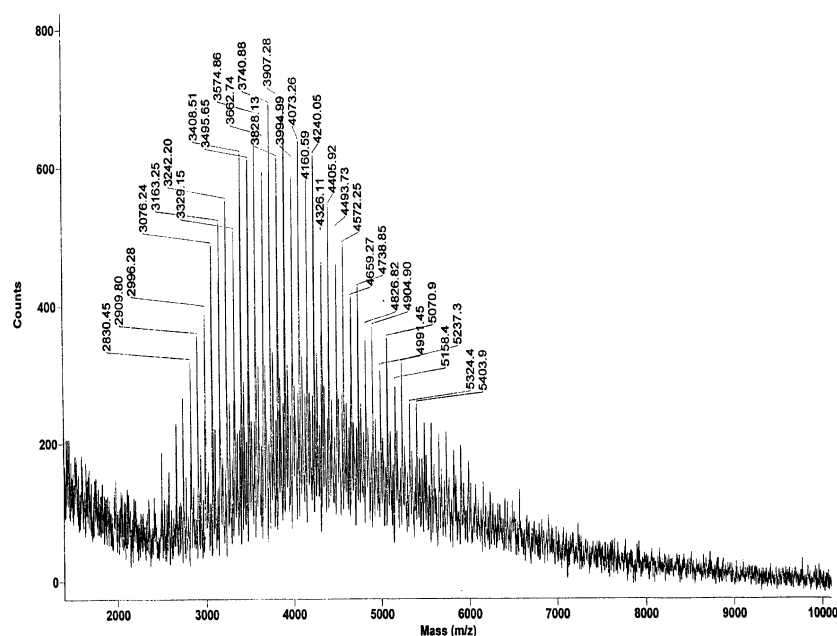


Fig. 3 MALDI-TOF-MS spectra of P3HT prepared in two steps.

solvents. In this context, we could not carry out the specific separation of high molecular weight fractions for all polymers. However, the ^1H -NMR spectra corresponding to the chloroform-soluble fractions of these 3-substituted polythiophenes are consistent with the spectra of the corresponding halogenated monomers, as reported in Fig. 4 for an ester-substituted polythiophene prepared in two steps.

These ^1H -NMR spectra show that alkyl protons corresponding to the ester group are recovered after polymerisation,

underlining the good functional compatibility of the method. The aromatic proton exhibits a broad resonance signal. As mentioned above, this does not imply that this polymer is regiorandom since its purification could be incomplete, the solid recovered being therefore a mixture of low and high molecular weight fragments.

In summary 2,5-dihalothiophenes substituted in the 3 position by a variety of functional groups undergo electro-reductive polymerisation either in one step using a nickel

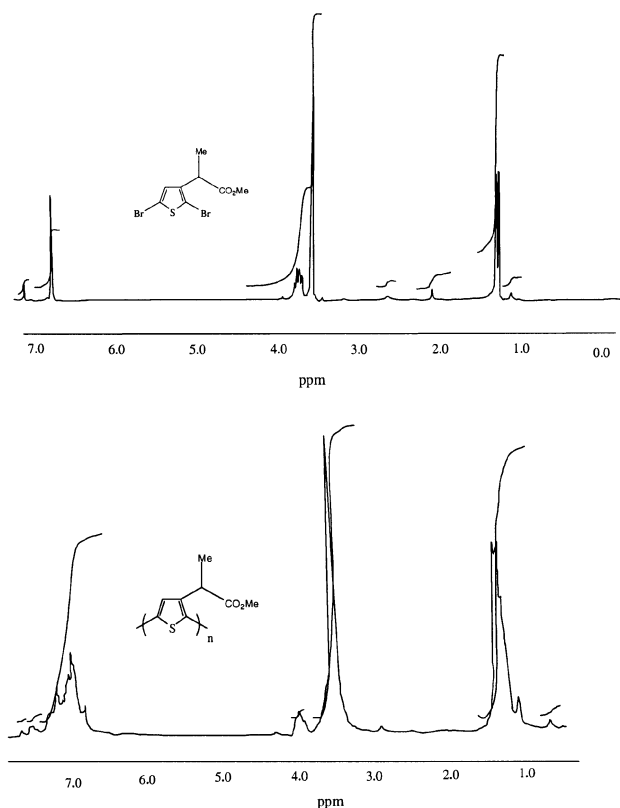


Fig. 4 ^1H -NMR spectra of the monomer and of poly(2-thiophen-3-yl-propionic acid methyl ester) prepared in two steps.

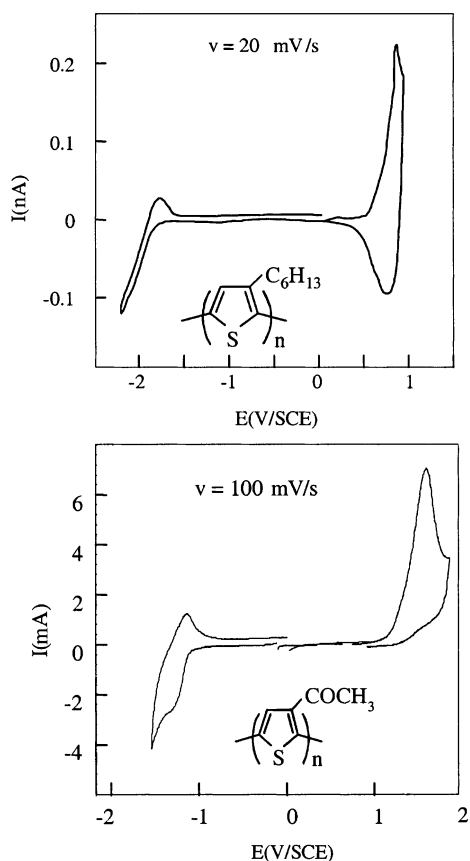


Fig. 5 Cyclic voltammograms in a 50 μm cavity Pt microelectrode of 3-substituted polythiophenes prepared in two steps. Solvent: acetonitrile with 0.1 mol dm^{-3} Bu_4NBF_4 .

Table 2 Electrochemical properties of 3-substituted polythiophenes prepared in one or two steps

Polymer	$E_{\text{ox}}/\text{V vs. SCE}$	$E_{\text{red}}/\text{V vs. SCE}$	Synthetic method
	1.14	—	1 step
	0.7–0.9	—	1 step
	0.5–0.7	–1.9	2 steps
	1.1	—	1 step
	0.8	–2	2 steps
	1.1	—	2 steps
	1.58	—	2 steps
	0.9	–1.56	2 steps
	1.5	–1.2	2 steps

^a Yield calculated vs. original 2,5-dihaloethiophene based on the mass of solid recovered, neglecting the mass of possible halogen end groups.

catalyst, or in two steps through the intermediate preparation of the corresponding thienylzinc species. The latter procedure leads to regioregular poly(3-alkylthiophenes) with well-defined structures.

Electrochemical properties

We have studied the electrochemical properties of the 3-substituted polythiophenes using “powder microelectrodes” (also called cavity microelectrodes), which are a very useful tool for the study of the redox properties of solid materials in the form of powders.¹⁶ Powders are introduced within the cavity of the electrode by pressing the electrode against the particles. As very small amounts of solid are necessary, this electrode technology allows high scan rates, especially compared to classical composite electrodes. The voltammograms of poly(3-hexylthiophene) and poly(3-acetylthiophene) prepared in two steps are reported in Fig. 5. Both p- and n-doping processes are observed for these polymers. Poly(3-hexylthiophene) exhibits a reversible reduction process at –2 V/SCE and its reversible oxidation takes place at 0.8 V/SCE. As the polymer is prepared in its neutral oxidation state (undoped), no counter-ions are incorporated during polymerisation. Thus, the polymer structure must be porous enough to allow their incorporation afterwards. Poly(3-acetylthiophene) reduces at –1.2 V/SCE and irreversibly oxidises at 1.5 V/SCE. This latter polymer is partially soluble in acetonitrile, and the shift in the potential values observed (with respect to the former polymer) are

consistent with the electronic effect of the acetyl substituent. The redox processes of the 3-substituted polythiophenes are reported in Table 2.

Most polymers exhibit p-doping processes, while n-doping was not systematically observed. The potential values are in agreement with both the conjugated structure of polythiophenes (bandgaps in the *ca.* 2.4–2.8 eV range) and with the electronic effect of the substituent.

Conclusions

Electrosynthetic procedures afford the one- or two-step preparation of 3-substituted polythiophenes for a wide range of functional groups. Poly(3-alkylthiophenes) prepared through the intermediate regioselective electrosynthesis of the corresponding thienylzinc species are regioregular. Moreover, polythiophenes prepared in this way exhibit well-defined p-doping processes, and in some cases n-doping is also observed. If the direct nickel-catalysed electroreductive polymerisation of 3-substituted 2,5-dihalo thiophenes is a much more straightforward route to the corresponding polythiophenes, the resulting polymers are much more polydispersed and/or regiorandom. The two-step electrochemical preparation of 3-substituted polythiophenes is a reliable method allowing a good functional compatibility.

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