Synthesis and electrochemical behaviour of new polythiophenes branched with sulfonamides for solid phase synthesis

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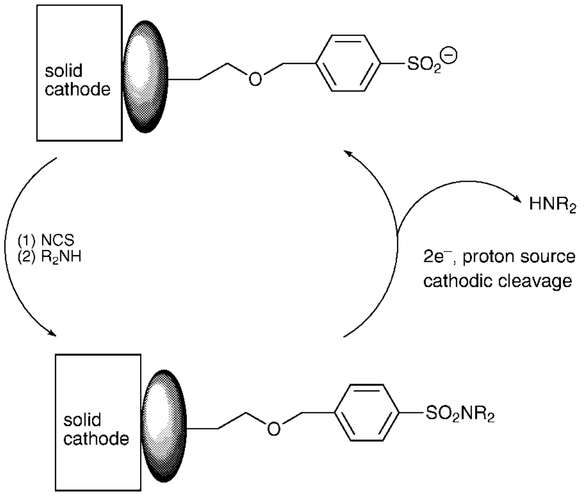
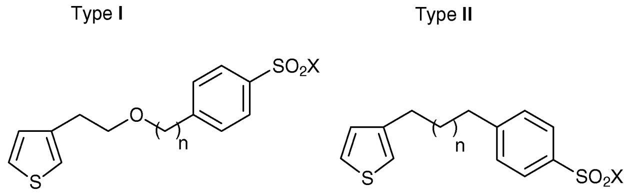
The synthesis of thiophenes 3-substituted by arylsulfonamide groups is described. Their electropolymerization and the characteristics of the polymers thus formed were studied, showing the importance of the nature of the spacer intercalated between the thiophene unit and the electroactive cleavable aromatic function under electron transfer. The presence of an oxygen atom in an appropriate position in the chain appears to dramatically control the electrochemical stability and the electroactivity of the polymer.

The tremendous activity devoted to combinatorial processes has focused mainly on the synthesis of new cleavable linkers such that product release from the solid support is more and more selective.[1] Thus, a wide range of cleavage reagents have been used, most were chemical[2] but the literature has also reported biochemical[3] or photochemical[4] processes. Additionally, the design or chemical engineering of new kinds of polymers or supported matrixes as alternatives to common beads has begun to be of increasing interest.[5] Thus, Pickett and coworkers[6] described the chemical reaction of active ester-substituted polypyrrole films with some amines leading to a functionalized resin possessing pendant amine groups.

In a previous work,[7] it has been shown that polythiophene films 3-functionalized with arylsulfonamide moieties could be used in a solid phase synthesis process (Scheme 1). The principle was originally based on an original and highly selective electrochemical release of various organic substrates from the cathodic cleavage of the S–N bond. Nevertheless, the feasibility of such a process was found to be very dependent on the stability of the polythiophene matrix.



Scheme 1



Ia$_1$ n = 0, X = NEt_2
Ia$_2$ n = 0, X = Me
Ib$_1$ n = 1, X = NEt_2
Ib$_2$ n = 1, X = Me

IIa$_1$ n = 0, X = NEt_2
IIa$_2$ n = 0, X = Me
IIb n = 1, X = NEt_2
IIc n = 2, X = NEt_2

Scheme 2

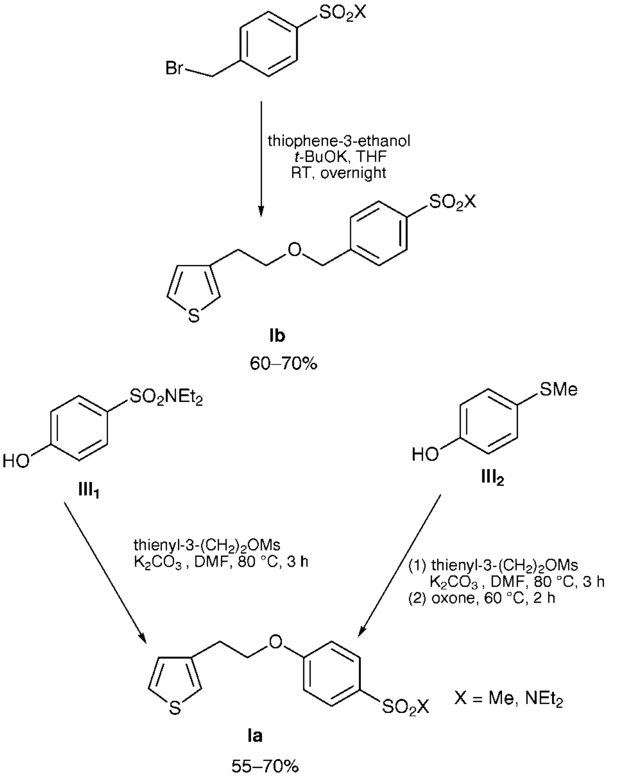
The present work deals with the synthesis of two classes of thiophene monomers, **I** and **II** (Scheme 2), both containing either a diethylphenylsulfonamide (**Ia$_1$**, **Ib$_1$**, **IIa$_1$**, **IIb**, **IIc**) or a methylphenylsulfone (**Ia$_2$**, **Ib$_2$**, **IIa$_2$**) unit as a cathodically electroactive function. As demonstrated by Garnier and coworkers,[8] some rules are a prerequisite for the successful electropolymerization of such thiophene monomers. Any steric or electron withdrawing effects must be as tiny as possible in order to allow thiophene unit anodic polymerization. As previously mentioned in the literature,[9] the length of the chain at the 3 position of the thiophene ring directs both the efficiency of the polymerization and the polymer conductivity. Thus, introduction of an alkyl chain as spacer in the 3 position affects drastically the polymerization reaction and the conductivity of the films. As a matter of fact, it was demonstrated that a spacer of at least three atoms prevented the steric hindrance and electron withdrawing effects of the phenyl groups as well as any intramolecular coupling.[8] Moreover, the devastating electron withdrawing effect of the oxygen atom in the vicinity of the thiophene can be neutralized by the intercalation of two or more methylene groups without any loss of polymer electroactivity. For all these reasons, the synthesis was focused on monomers with a linear spacer containing 2 to 4 atoms. Moreover, in order to maintain a sufficient electroactivity level of the poly**I** matrix, the position of the oxygen atom in the spacer of type **I** derivatives was located as far as possible from the thiophene ring.[10]

In this paper we report the synthesis of various precursors and the study of their polymers.

Results and discussion

Synthesis of monomers

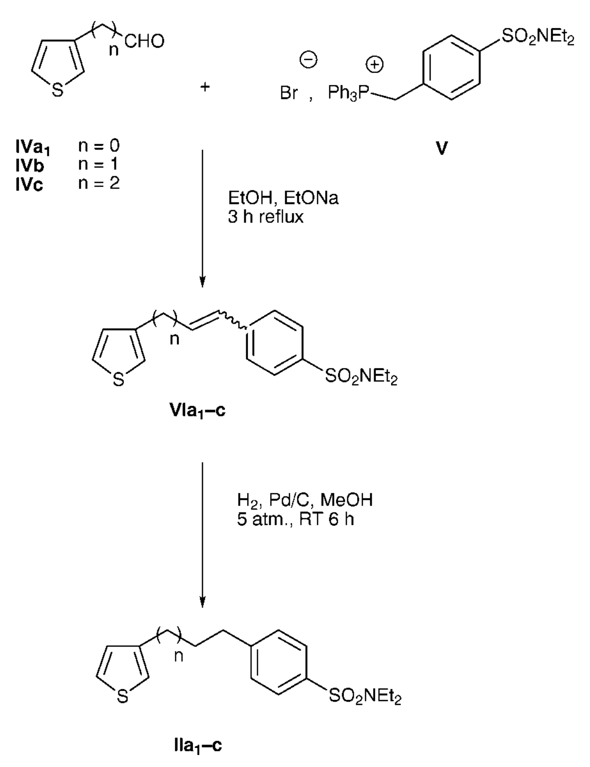
All type **I** monomers were synthesized by two main approaches. The first one, previously described,[7] consists of a thiophene alkoxide condensation on bromobenzyl species. Compounds **Ia** were readily obtained by the second route involving a phenoxide nucleophilic substitution onto a thiophene mesylate[11] (Scheme 3). Thus, on the one hand, 4-methylsulfanyl phenol, **III$_2$**,[12] was reacted with 2-(3-thienyl)-ethylmesylate under basic conditions leading after gentle oxidation[13] to **Ia$_2$**. On the other hand, the **Ia$_1$** derivative was obtained under similar experimental conditions from *p*-hydroxyphenyldiethylsulfonamide, **III$_1$**.[14]



Scheme 3

The type **II** target compounds were obtained from two different approaches, depending on the nature of the phenyl substitution. Thus, diethyl sulfonamide derivatives **IIa$_1$,b,c** (Scheme 4) were prepared in good yields through a Wittig reaction followed by homogeneous catalytic hydrogenation. Aldehydes **IVa$_1$,b,c**, synthesized according to known procedures,[15] were reacted with triphenylphosphonium bromide **V**, yielding 45–60% of a *cis-trans* isomer mixture. Moreover, concomitantly to the alkene formation, a side reaction occurred due to instability[16] of the phosphonium salt **V**, which rendered product purification delicate. As expected, the *cis* : *trans* isomer ratio was directly linked to the length of the spacer. Whereas the *trans* isomer only was detected when a short spacer was involved (for **VIa$_1$**), increasing amounts of the *cis* derivative appeared with longer ones (30% and 50% respectively for **VIb** and **VIc**). This could be explained by the hindrance of the bulky diethylphenylsulfonamide moiety, which tends to decrease with a longer chain. Finally, a smooth hydrogenation of the *cis-trans* alkene mixture over deactivated palladium afforded high yields of the corresponding monomers.

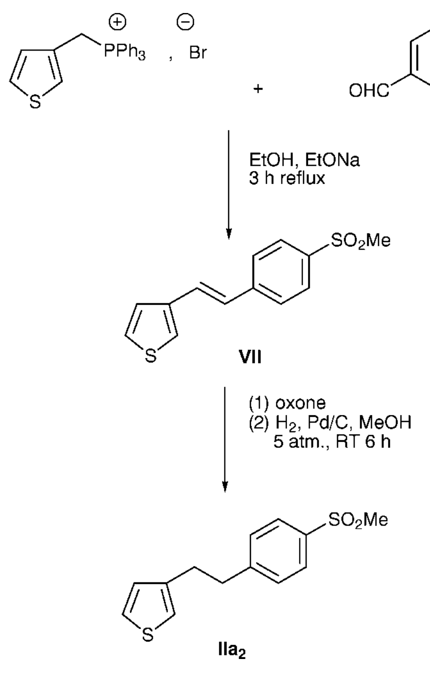
Similarly, the methyl sulfone **IIa$_2$** was prepared from *p*-methylthiobenzaldehyde and thienyl methyl triphenylphosphonium bromide (Scheme 5).[17] The intermediate alkene thus formed was found to be pure *trans* isomer, correlating to previous observations.



Scheme 4

Electroformation of 3-substituted polythiophene films

All studied monomers showed two irreversible anodic peaks, more or less differentiated depending on the nature of the phenyl substitution. They were found to electrochemically polymerize within the anodic range either by repetitive scans (Fig. 1) or potentiostatically (Fig. 2). As a matter of fact, when methyl sulfone derivatives were involved (entries 2, 4 and 6 in Table 1) the first peak potential of the monomers was more anodic than the one observed with diethylsulfonamide compounds (entries 1, 3, 5, 7 and 8). This experimental fact can be explained by an inductive effect of the more electron withdrawing methylsulfone group.[18] The second peak has been assigned to the over-oxidation of the preformed polymer as a second scan up to this potential evidenced a passivation phenomenon of the electrode surface. Moreover, the nature of the



Scheme 5

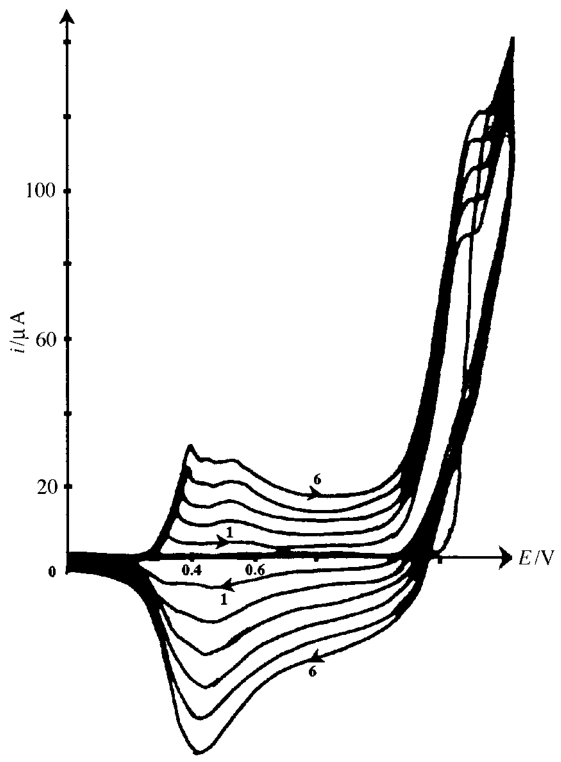


Fig. 1 Electroformation of poly**Ib**$_1$ (28 mM **Ib**$_1$ in CH_3CN + 0.1 M Bu_4NBF_4) at a stationary Pt (1 mm diameter) electrode for the six first sweeps between 0 and 1.35 V. Scan rate 100 mV s^{-1}. Reference 0.1 M acetonitrile Ag/Ag$^+$ solution.

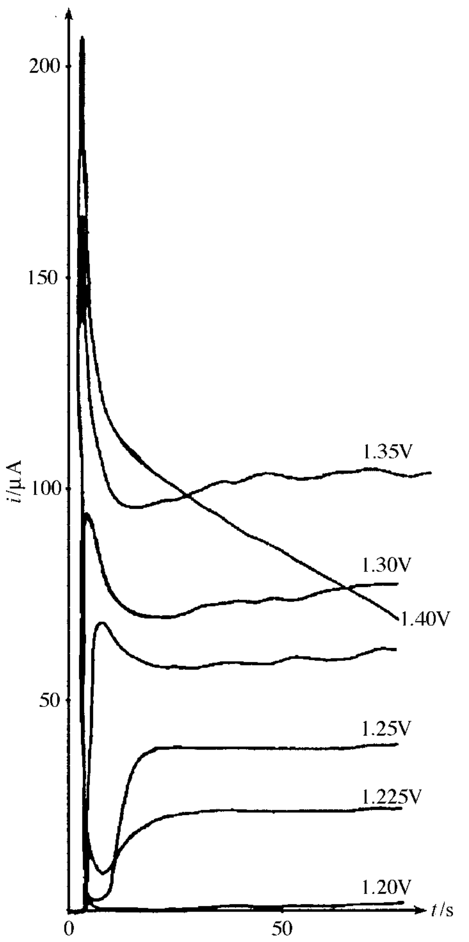


Fig. 2 Chronoamperometric plots of 28 mM **Ib**$_1$ at different potential values at a stationary Pt (1 mm diameter) electrode.

Table 1 Anodic peak potentials (E_{pa1} and E_{pa2}) of monomers and electroformation potentials (E_f) of their corresponding polymers, in CH_3CN + 0.1 M Bu_4NBF_4

Entry	Monomer	E_{pa1}/V	E_{pa2}/V	E_f/V
1	**Ia**$_1$	1.50	1.73	1.35
2	**Ia**$_2$	1.60	1.77	1.35
3	**Ib**$_1$	1.48	1.68	1.30
4	**Ib**$_2$	1.52	1.74	1.35
5	**IIa**$_1$	1.50	1.68	1.40
6	**IIa**$_2$	1.55	1.87	1.40
7	**IIb**	1.50	1.68	1.45
8	**IIc**	1.54	—	1.40

Scan rate 100 mV s^{-1}. Reference 0.1 M acetonitrile Ag/Ag$^+$ solution.

spacer did not seem to have any significant influence on the first peak potential. A surprising feature concerns the behaviour of **IIc** (Table 1, entry 8). A correlation between the electrochemical instability of the polymer and the fact that only one anodic peak was observed for the monomer (Fig. 3) must be pointed out. The overlapping of the peaks (attributed respectively to the monomer oxidation and the preformed polymer over-oxidation) must also be noticed. Thus, whatever the electroformation potential (E_f) value applied, the instability is probably caused by an over-oxidation of the first deposited layers during polymer formation. In particular, this

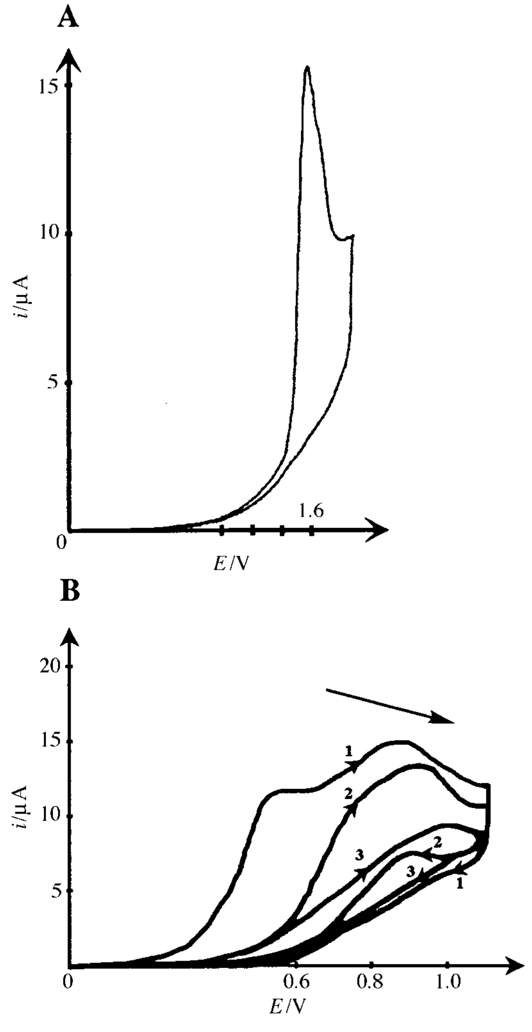


Fig. 3 (*A*) Cyclic voltammogram of monomer **IIc** (2.8 mM in 0.1 M Bu_4NBF_4 + CH_3CN) at a Pt electrode, scan rate 100 mV s^{-1}. (*B*) Cyclic voltammogram of poly**IIc** in 0.1 M Bu_4NBF_4 + CH_3CN. Deposition charge 1 mC mm^{-2} on Pt, scan rate 100 mV s^{-1}.

has already been noticed for other type **Ia** monomers that have no substituents on the phenyl.[19]

Scanning electron microscopy (SEM) analysis of the polymers revealed a remarkably smooth surface of the film (Fig. 4), contrary to what is observed for most polythiophenes.[20] This phenomenon is consistent with a progressive and uniform electropolymerization process for $\mathbf{Ib_1}$ derivatives as no disruption at the film surface was detectable. Furthermore, as previously mentioned in the literature,[21] the appearance of grains [especially as exhibited in Fig. 4(*B*)] in the polymer bulk could be assigned to the tetrabutylammonium tetrafluoroborate salt, which is strongly retained during the electrosynthesis step.

Behaviour of polyI-II derivatives: electrochemical dependence on their structure

The polymers' electrochemical stability has been tested by means of continuous cycling between 0 and +1 V (6 cycles).

The first characteristic examined concerned the dependence of the redox potentials of poly**I** and **II** on the presence of an ether function in the spacer. Results (Table 2) showed that two anodic steps (located at E_{pa_1} and E_{pa_2}) were distinguished in almost all cases. Both poly**Ia** exhibited oxidation potentials higher than these of poly**Ib**. The latter values were related to the donor mesomer effect of the oxygen atom directly attached to the phenyl ring. Moreover, as already reported by Roncali *et al.*[9] for thiophenes 3-substituted with open diether chains, it was observed that the oxidation potential of poly**Ib** appeared significantly lower than that of the alkyl analogues. The presence of an ether linkage thus neutralizes steric effects associated with *n*-alkyl spacers on the electrochemical properties of the polymer. It was also shown that E_{pa} of poly$\mathbf{IIa_1}$ was slightly higher than that determined for poly**IIb**, due to the larger steric hindrance caused by the phenyl group, which lowered the intrachain conductivity. Furthermore, the difference between poly**IIb** and poly**IIc** was ascribed to the length of the alkyl spacers, which tend to decrease the interchain contact. Lastly, the specific polar effect of the linkage obviously brings a better solvation by acetonitrile and activates charge mobility within the resin.

On the other hand, contrary to a proposal by Roncali *et al.*,[22] it was observed that the phenyl ring substitution exerts a noticeable electronic effect on the conjugated backbone since the E_{pa} values of poly$\mathbf{Ib_2}$ (sulfone species) are higher than for poly$\mathbf{Ib_1}$ (sulfonamide species).

Additionally, we focused our attention on the p-doping level of the poly**I** and **II** films. The regularity of their tertiary structure has been shown to affect strongly the polymer p-doping value in controlling the insertion of the doping counter-anions. Table 3 gathers the calculated p-doping level values of the relevant polymers. The poly**Ia** and **Ib** films exhibit a greater p-doping level than the poly**II** ones (Fig. 5). This increase in doping is explained by the rigidity of the spacer in the polymers. It was thus assumed that a more rigid linker (such as the oxyalkyl chain in poly**I** films) led to a tertiary matrix structure with larger pores caused by repulsive effects between heteroatoms. This should allow an easy in-out process of the electrolyte, thus increasing the doping level (Table 3, entries 1–4). In contrast, when an alkyl chain is involved (Table 3, entries 5–8), porosity decreases, which explains the lower p-doping level values calculated for poly**II** films. Moreover, in the latter case a progressive shift (see Fig. 5, **IIb**) towards more positive potentials during the voltammetric steps was observed, which demonstrates the decrease of the stability and electroactivity of poly**IIb**. This is explained by a partial dedoping (*i.e.* anion trapping, helped by the

Table 2 Cyclic voltammetry data of different polymers deposited on a Pt disk electrode, in $CH_3CN + 0.1$ M Bu_4NBF_4

Entry	Polymer	E_{pa1}/V	E_{pa2}/V	E_{pc}/V
1	Poly$\mathbf{Ia_1}$	0.54	0.62	0.52
2	Poly$\mathbf{Ia_2}$	0.62	—	0.48
3	Poly$\mathbf{Ib_1}$	0.37	0.55	0.50
4	Poly$\mathbf{Ib_2}$	0.50	0.65	0.56
5	Poly$\mathbf{IIa_1}$	0.46	0.55	0.52
6	Poly$\mathbf{IIa_2}$	0.53	—	0.56
7	Poly**IIb**	0.42	0.52	0.45
8	Poly**IIc**	0.52	0.86	0.64

Scan rate 100 mV s^{-1}.

Table 3 p-Doping level of different electroformed polymers

Entry	Polymer	p-doping level[a] (%)
1	poly$\mathbf{Ia_1}$	17.1
2	poly$\mathbf{Ia_2}$	16.5
3	poly$\mathbf{Ib_1}$	23.9
4	poly$\mathbf{Ib_2}$	17.7
5	poly$\mathbf{IIa_1}$	11.1
6	poly$\mathbf{IIa_2}$	11.8
7	poly**IIb**	11.0
8	poly**IIc**	8.5

[a] This parameter was estimated electrochemically from the ratio $2Q_a/(Q_f - Q_a)$ where Q_f is the electroformation charge of the polymer and Q_a is the anodic charge corresponding to the p-doping process determined by integration of the cyclic voltammetry curve. The electropolymerization yield was assumed to be quantitative.

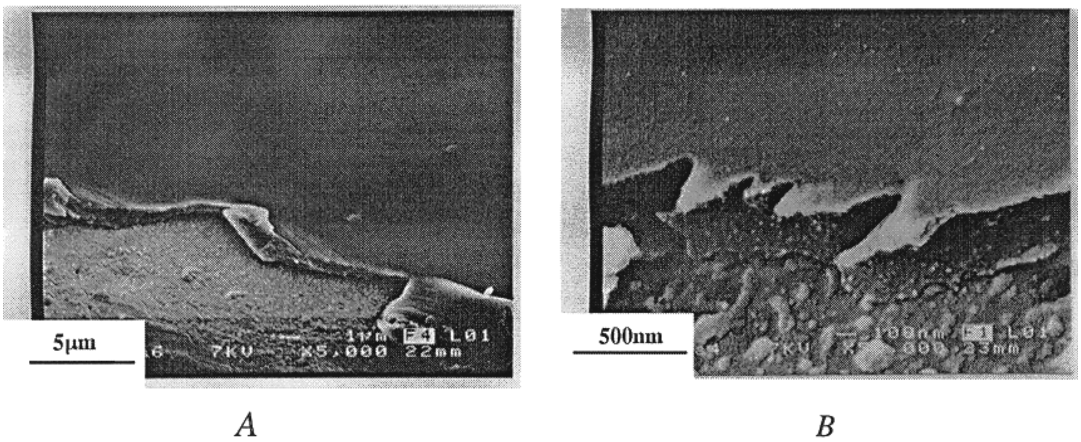


Fig. 4 SEM micrographs of a poly$\mathbf{Ib_1}$ sample deposited on a Pt sheet (upper part of each slide). Deposition charge 1 mC mm^{-2} at 1.35 V.

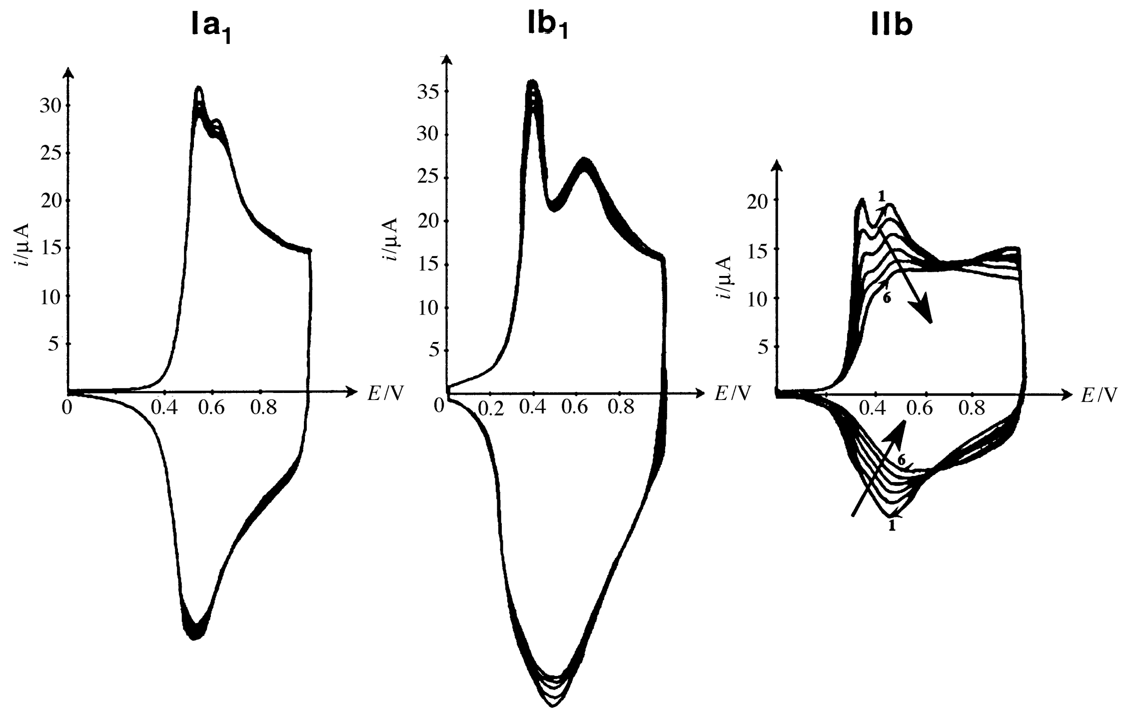


Fig. 5 Cyclic voltammograms of polythiophenes in 0.1 M Bu_4NBF_4 + CH_3CN. Deposition charge 1 mC mm^{-2} on Pt (28 mM of monomer), scan rate 100 mV s^{-1}.

higher criss-cross of the polymer matrix) due to a faster reorganization of the polymer matrix during the process.

Thus, the electrochemical stability and the electroactivity of the polymers containing alkyloxy spacers is found to be better than those with flexible alkyl chains.

Conclusions

The results given in this article indicate the role of both the nature of the spacer and the phenyl substitution towards the electrosynthesis and the electrochemical stability of the designed functional poly**I** and **II**. While the nature of the spacer does not exhibit any significant influence on the monomer oxidation, it appears to dramatically affect both the redox potential and the electrochemical stability of the polymer. Thus, easier polymer oxidation was observed when an oxygen atom (compared to a carbon atom) was introduced at the benzylic position in the linker chain. In contrast, the opposite effect was observed when the oxygen atom was directly grafted onto the phenyl ring, illustrating the steric effect induced by the substitution on the thiophene ring and also a noticeable electron donor effect of the oxygen on the phenyl group. Moreover, the structure of the polymer was found to strongly influence the p-doping level value. Thus, the relative rigidity of the alkyloxy spacer could lead to a better organization of the matrix, facilitating the in-out anion flux during the p-doping process, contrary to alkyl linkers where anion trapping was observed.

By an appropriate choice of spacer, stable 3-functionalized polythiophenes showing improved electrochemical stability have been synthesized, which, in combination with their chemical stability,[7] can be engaged in heterogeneous synthesis.

Experimental

All organic reactions were carried out under a nitrogen atmosphere. Organic solvents were freshly distilled over Na or P_2O_5 before use. Light petroleum refers to the 40–60 °C fraction. All solvents for electrochemical studies were purchased from SDS with less than 100 ppm of water and stored under argon. Tetrabutylammonium tetrafluoroborate from Fluka was recrystallized three times from methanol–water (1 : 1) and dried for 48 h under vacuum. Aluminium oxide was activated by heating at 450 °C under vacuum for 24 h and used at once under argon pressure. A carbon rod electrode was used as counter electrode and a 0.1 M acetonitrile Ag/Ag^+ solution was used as reference electrode.

The three-electrode cell was connected to a PAR model 173 potentiostat monitored with a PAR model 175 signal generator and a PAR model 179 digital coulometer. The cyclic voltammetry traces were recorded on an XY SEFRAM-type TGM 164.

^1H and ^{13}C NMR investigations were performed on a Bruker AC 300 spectrometer, in deuteriochloroform, using TMS as internal reference. Melting points were determined on an Electrothermal® melting point apparatus. Silica gel (70–230 mesh) for column chromatography was purchased from Merck.

Synthesis of type Ia monomers

To a well stirred suspension of $\mathbf{III_1}$ (1.6 mmol) in anhydrous DMF (10 ml) was slowly added potassium carbonate (1.6 mmol) at room temperature. The solution was heated at 80 °C until potassium carbonate had been consumed and the mesylate (300 mg, 1.45 mmol) in anhydrous DMF (5 ml) was added. After 3 h, the reaction mixture was cooled by pouring into water (25 ml) and extracted twice with 50 ml methylene chloride. The combined organic layers were washed with a saturated ammonium chloride solution, dried over anhydrous sodium sulfate, concentrated to dryness and purified by column chromatography (light petroleum–ether 1 : 1) giving the desired monomer.

$\mathbf{Ia_1}$: white oil. Yield: 54%. ^1H NMR: 7.72 and 6.95 (4H, AB system, $^3J_{HH} = 8.9$ Hz, H_{arom}); 7.28 (1H, dd, $^4J_{HH} = 3.1$ Hz, $^3J_{HH} = 4.7$ Hz, $H_{thiophene}$); 7.09 (1H, m, $H_{thiophene}$); 7.03 (1H, dd, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 4.7$ Hz, $H_{thiophene}$); 4.21 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2O); 3.20 (4H, q, $^3J_{HH} = 7.2$ Hz, CH_2N); 3.14 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene); 1.11 (6H, t, $^3J_{HH} = 7.2$ Hz). ^{13}C NMR: 161.83, 138.00, 132.15 (C_{arom}); 129.10, 114.70 (CH_{arom}); 128.10, 125.70, 121.80 ($CH_{thiophene}$);

68.40 (CH_2O); 42.00 (CH_2N); 30.10 (CH_2-thiophene); 14.20 (CH_3). $M^{+\cdot}$ required: 339.0963; found: 339.0960. $C_{16}H_{21}NO_3S_2$ required: C, 56.6; H, 6.2; found: C, 56.5; H, 6.3.

For **Ia$_2$** the same procedure as described for **Ia$_1$** was employed starting from **III$_2$** (1.6 mmol) leading to the desired alkene sulfide intermediate. Yellow oil. Yield: 70%. ^1H NMR: 7.22 and 6.81 (4H, AB system, $^3J_{HH} = 8.8$ Hz, H_{arom}); 7.22 (1H, m, $H_{thiophene}$); 7.03 (1H, m, $H_{thiophene}$); 6.98 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 4.09 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2O); 3.06 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene); 2.39 (3H, s, CH_3). ^{13}C NMR: 157.25, 138.30, 128.90 (C_{arom}); 130.00, 115.20 (CH_{arom}); 128.40, 125.40, 121.50 ($CH_{thiophene}$); 68.10 (CH_2O); 30.10 (CH_2-thiophene); 17.86 (CH_3).

This sulfide (240 mg, 0.96 mmol) was oxidized by addition to a vigorously stirred suspension of wet alumina (953 g) and oxone (1.76 g, 2.86 mmol) in chloroform (5 ml). The mixture was heated at reflux until all starting material and sulfoxide had been consumed. The mixture was then cooled and filtered. The filtrate was dried over anhydrous sodium sulfate and concentrated to dryness. The obtained solid was purified by column chromatography (light petroleum–ether 1 : 2) to give the expected monomer.

Ia$_2$: white solid. Quantitative yield. Mp: 46 °C. ^1H NMR: 7.85 and 7.01 (4H, AB system, $^3J_{HH} = 8.9$ Hz, H_{arom}); 7.28 (1H, dd, $^4J_{HH} = 3.0$ Hz, $^3J_{HH} = 4.8$ Hz, $H_{thiophene}$); 7.09 (1H, m, $H_{thiophene}$); 7.03 (1H, m, $H_{thiophene}$); 4.24 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2O); 3.15 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene); 3.01 (3H, s, CH_3). ^{13}C NMR: 161.90, 136.80, 131.30 (C_{arom}); 128.50, 113.90 (CH_{arom}); 127.30, 124.70, 120.80 ($CH_{thiophene}$); 63.10 (CH_2O); 43.80 (CH_3); 28.90 (CH_2-thiophene). $M^{+\cdot}$ required: 282.0384; found: 282.0393. $C_{13}H_{14}O_3S_2$ required: C, 55.3; H, 5.0; O, 17.0; S, 22.7; found: C, 54.8; H, 5.1; O, 17.4, S, 22.4.

Synthesis of type Ib monomers

To a well stirred suspension of thiophene-3-ethoxide (4.31 mmol) prepared from potassium *tert*-butoxide (4.7 mmol) and thiophene-3-ethanol in 20 ml anhydrous THF, was slowly added at room temperature a 5 ml THF solution of *p*-bromomethylphenylsulfone or diethylsulfonamide (3.92 mmol). After stirring overnight, the yellow-orange reaction mixture was poured into water (25 ml) and extracted twice with 50 ml methylene chloride. The combined organic layers were washed with water (20 ml), dried over anhydrous sodium sulfate, concentrated to dryness and purified by column chromatography (light petroleum–ether 1 : 2) giving the expected monomers.

Ib$_1$: colourless liquid. Yield: 60%. ^1H NMR: 7.70 and 7.31 (4H, AB system, $^3J_{HH} = 8.3$ Hz, H_{arom}); 7.17 (1H, dd, $^4J_{HH} = 3.0$ Hz, $^3J_{HH} = 4.9$ Hz, $H_{thiophene}$); 6.95 (1H, dd, $^4J_{HH} = 3.0$ Hz, $^4J_{HH} = 1.1$ Hz, $H_{thiophene}$); 6.90 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.1$ Hz, $H_{thiophene}$); 4.50 (2H, s, $PhCH_2O$); 3.65 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2O); 3.15 (4H, q, $^3J_{HH} = 7.1$ Hz, CH_2N); 2.89 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene); 1.04 (6H, t, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C NMR: 143.20, 139.30, 139.00 (C_{arom}); 127.60, 127.10 (CH_{arom}); 128.45, 125.40, 121.30 ($CH_{thiophene}$); 72.00 ($PhCH_2O$); 71.00 (CH_2O); 42.10 (CH_2N); 30.70 (CH_2-thiophene); 14.2 (CH_3). $M^{+\cdot}$ required: 353.1119 found: 353.1112. $C_{17}H_{23}NO_3S_2$ required: C, 57.8; H, 6.6; N, 3.9; O, 13.6; S, 18.1; found: C, 57.9; H, 6.5; N, 3.9; O, 13.7; S, 18.1.

Ib$_2$: white solid. Yield: 70%. Mp: 48 °C. ^1H NMR: 7.83 and 7.42 (4H, AB system, $^3J_{HH} = 8.4$ Hz, H_{arom}); 7.20 (1H, dd, $^4J_{HH} = 2.8$ Hz, $^3J_{HH} = 4.9$ Hz, $H_{thiophene}$); 6.97 (1H, dd, $^4J_{HH} = 2.8$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 6.91 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 4.54 (2H, s, $PhCH_2O$); 3.66 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2O); 2.97 (3H, s, CH_3SO_2); 2.91 (2H, t, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene). ^{13}C NMR: 152.65, 147.17, 146.63 (C_{arom}); 135.50, 135.16 (CH_{arom}); 136.10, 133.10, 128.97 ($CH_{thiophene}$); 79.50 ($PhCH_2O$); 78.70 (CH_2O); 52.20 (CH_3SO_2); 38.37 (CH_2-thiophene). $M^{+\cdot}$ required: 296.0541; found: 296.0537. $C_{14}H_{16}O_3S_2$ required: C, 56.8; H, 5.4; O, 16.2; S, 21.7; found: C, 56.9; H, 5.4; O, 16.1; S, 21.8.

Synthesis of type II monomers

Wittig's reaction. To a well stirred suspension of phosphonium salt (2.5 mmol), aldehyde (2.5 mmol) and absolute ethanol (12 ml) at 60 °C, was slowly added a solution of 0.4 M sodium ethoxide in ethanol (3 ml). The immediate precipitation of a yellow solid was observed. After 3 h at reflux, the reaction mixture was poured into water (25 ml) and extracted twice with 50 ml methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulfate, concentrated to dryness and purified by column chromatography (light petroleum–ether 4 : 1) giving the monomer.

VII: yellow solid. Yield: 42%. ^1H NMR: 7.40–6.49 (9H, m, H_{arom}, $H_{thiophene}$, H_{vinyl}); 2.47 (3H, s, CH_3S). ^{13}C NMR: 138.27, 137.41, 134.45 (C_{arom}); 129.28, 126.73 (CH_{arom}); 128.95, 128.02 (CH_{vinyl}); 126.77, 125.04, 124.27 ($CH_{thiophene}$); 15.69 (CH_3).

VIa$_1$: yellow solid. Yield: 60%. ^1H NMR: 7.71 and 7.40 (4H, AB system, $^3J_{HH} = 8.4$ Hz, H_{arom}); 7.15 (1H, dd, $^4J_{HH} = 3$ Hz, $^3J_{HH} = 4.9$ Hz, $H_{thiophene}$); 7.11 (1H, dd, $^4J_{HH} = 3$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 6.79 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 6.65 and 6.53 (2H, AB system, $^3J_{HH\,trans} = 12.2$ Hz, H_{vinyl}); 3.25 (4H, q, $^3J_{HH} = 7.15$ Hz, CH_2N); 1.13 (6H, t, $^3J_{HH} = 7.15$ Hz). ^{13}C NMR: 142.02, 138.83, 137.45 (C_{arom}); 129.31, 127.00 (CH_{arom}); 127.62 (CH_{vinyl}); 126.62, 125.45, 124.86 ($CH_{thiophene}$); 42.00 (CH_2N); 14.10 (CH_3).

VIb: yellow oil. Yield: 59%. Mixture of *cis* and *trans* (30/70) isomers. *trans*: ^1H NMR: 7.74 and 7.35 (4H, AB system, $^3J_{HH} = 8.3$ Hz, H_{arom}); 7.26 (1H, dd, $^4J_{HH} = 3$Hz, $^3J_{HH} = 4.8$ Hz, $H_{thiophene}$); 7.18 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 7.11 (1H, dd, $^4J_{HH} = 3$ Hz, $^4J_{HH} = 1.2$ Hz, $H_{thiophene}$); 6.47 (1H, m, H_{vinyl}); 6.16 (1H, dt, $^3J_{HH\,trans} = 15.7$ and 6.8 Hz, H_{vinyl}); 3.56 (2H, d, $^3J_{HH} = 6.8$ Hz, CH_2-thiophene); 3.23 (4H, q, $^3J_{HH} = 7.1$ Hz, CH_2N); 1.13 (6H, t, $^3J_{HH} = 7.1$ Hz). *cis*: ^1H NMR: 7.72 and 7.44 (4H, AB system, $^3J_{HH} = 8.4$ Hz, H_{arom}); 7.29 (1H, dd, $^4J_{HH} = 3$ Hz, $^3J_{HH} = 4.8$ Hz, $H_{thiophene}$); 7.01 (1H, dd, $^4J_{HH} = 3$ Hz, $^4J_{HH} = 1$ Hz, $H_{thiophene}$); 6.97 (1H, dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 1$ Hz, $H_{thiophene}$); 6.47 (2H, m, H_{vinyl}); 3.58 (2H, d, $^3J_{HH} = 6.8$ Hz, CH_2); 3.23 (4H, q, $^3J_{HH} = 7.1$ Hz, CH_2N); 1.12 (6H, t, $^3J_{HH} = 7.1$ Hz).

VIc: yellow oil. Yield: 53%. Mixture of *cis* and *trans* (50/50) isomers. ^1H NMR: 7.76–6.91 (7H, m, H_{arom}, $H_{thiophene}$); 6.49–5.75 (2H, m, $H_{vinyl\,cis/trans}$); 3.22 (4H, m, 2 CH_2N); 2.80 (2H, m, CH_2); 2.60 (2H, m, CH_2); 1.11 (6H, m, CH_3).

Oxidation. The alkene methylsulfone intermediate was prepared according to an approach similar to that developed for **Ia$_2$**. White solid. Quantitative yield. ^1H NMR: 7.77 and 7.50 (4H, AB system, $^3J_{HH} = 8.3$ Hz, H_{arom}); 7.17 (2H, m, $H_{thiophene}$); 6.82 (1H, dd, $^3J_{HH} = 4.6$ Hz, $^4J_{HH} = 1.6$ Hz, $H_{thiophene}$); 6.69 and 6.53 (2H, AB system, $^3J_{HH\,trans} = 12.2$ Hz, H_{vinyl}); 3.03 (3H, s, CH_3S).

Alkene reduction. A well stirred and purged under N_2 solution of **VI** or the previous methylsulfone derivative (1 mmol) in methanol (10 ml) was hydrogenated under hydrogen pressure (5 atm) in the presence of 0.1 mmol of 10% Pd/C. After 6 h, the mixture was filtered through celite. The celite was washed with methanol and the filtrate was concentrated to dryness and purified by column chromatography (light petroleum–ethyl acetate 4 : 1 for sulfonamide or light petroleum–ether 1 : 2 for sulfone), giving the expected monomer.

IIa$_1$: yellow solid. Yield: 80%. Melting point: 56–57 °C. ^{1}H NMR: 7.60 and 7.16 (4H, AB system, $^3J_{HH} = 8.4$ Hz, H$_{arom}$); 7.13 (1H, dd, $^4J_{HH} = 3$ Hz, $^3J_{HH} = 4.85$ Hz, H$_{thiophene}$); 6.78 (2H, m, H$_{thiophene}$); 3.15 (4H, q, $^3J_{HH} = 7.15$ Hz, CH$_2$N); 2.87 (4H, m, CH$_2$CH$_2$); 1.01 (6H, t, $^3J_{HH} = 7.15$ Hz). ^{13}C NMR: 146.50, 141.20, 137.95 (C$_{arom}$); 129.10, 127.20 (CH$_{arom}$); 128.10, 125.55, 120.70 (CH$_{thiophene}$); 42.00 (CH$_2$N); 36.70 (CH$_2$); 31.67 (CH$_2$); 14.20 (CH$_3$). $M^{+\cdot}$ required: 323.1014; found: 323.1020.

IIa$_2$: yellow solid. Yield: 80%. Melting point: 105 °C. ^{1}H NMR: 7.74 and 7.25 (4H, AB system, $^3J_{HH} = 8.1$ Hz, H$_{arom}$); 7.15 (1H, dd, $^4J_{HH} = 3$ Hz, $^3J_{HH} = 4.6$ Hz, H$_{thiophene}$); 6.82 (2H, m, H$_{thiophene}$); 2.94 (3H, s); 2.89 (4H, m, 2CH$_2$). ^{13}C NMR: 148.20, 141.00, 138.20, (C$_{arom}$); 128.00, 125.68, 120.77 (CH$_{thiophene}$); 129.50, 127.45 (CH$_{arom}$); 44.60 (CH$_3$SO$_2$); 36.80 (CH$_2$); 31.60 (CH$_2$). $M^{+\cdot}$ required: 266.0435; found: 266.0440.

IIb: yellow oil. Yield: 80%. ^{1}H NMR: 7.62 and 7.19 (4H, AB system, $^3J_{HH} = 8.3$ Hz, H$_{arom}$); 7.15 (1H, m, H$_{thiophene}$); 6.83 (2H, m, H$_{thiophene}$); 3.13 (4H, q, $^3J_{HH} = 7.1$ Hz, CH$_2$N); 2.60 (2H, t, $^3J_{HH} = 7.5$ Hz, CH$_2$); 2.57 (2H, t, $^3J_{HH} = 7.6$ Hz, CH$_2$); 1.87 (2H, quint, $^3J_{HH} = 7.6$ Hz, CH$_2$); 1.02 (6H, t, $^3J_{HH} = 7.1$ Hz). ^{13}C NMR: 147.20, 142.10, 137.75 (C$_{arom}$); 129.06, 127.10 (CH$_{arom}$); 128.10, 125.50, 120.30 (CH$_{thiophene}$); 42.10 (CH$_2$N); 35.20 (CH$_2$); 31.72 (CH$_2$); 29.66 (CH$_2$); 14.22 (CH$_3$). $M^{+\cdot}$ required: 337.1170; found: 337.1168.

IIc: yellow oil. Yield: 80%. ^{1}H NMR: 7.69 and 7.27 (4H, AB system, $^3J_{HH} = 8.3$ Hz, H$_{arom}$); 7.23 (1H, dd, $^4J_{HH} = 3.2$ Hz, $^3J_{HH} = 4.7$ Hz, H$_{thiophene}$); 6.90 (2H, m, H$_{thiophene}$); 3.22 (4H, q, $^3J_{HH} = 7.1$ Hz, CH$_2$N); 2.66 (4H, m, 2 CH$_2$); 1.66 (2H, m, 2 CH$_2$); 1.05 (6H, t, $^3J_{HH} = 7.1$ Hz). ^{13}C NMR: 147.50, 142.60, 137.70 (C$_{arom}$); 129.10, 127.10 (CH$_{arom}$); 128.10, 125.35, 120.00 (CH$_{thiophene}$); 42.10 (CH$_2$N); 35.60 (CH$_2$); 30.60 (CH$_2$); 30.50 (2 CH$_2$); 14.22 (CH$_3$). $M^{+\cdot}$ required: 351.1327; found: 351.1366.

Anodic polymerization of monomers

All electrochemical polymerizations of monomers were achieved under argon atmosphere in a three-electrode cell with a reaction medium containing an acetonitrile solution of 0.1 M NBu$_4$BF$_4$ and 0.028 M of monomer. Polymers were grown under a constant potential on a platinum electrode by using a global deposition charge of 1 mC mm^{-2}. After polymerization, the films were thoroughly rinsed with acetonitrile and transferred for further analytical studies into a monomer-free electrolyte.

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