Control of the Bandgap of Conducting Polymers by Rigidification of the π-Conjugated System

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Rigidification of *E*-1,2(2,2′-dithienylethylene) by bridging the thiophene rings with the central double bond leads to a *ca.* 0.40 eV decrease of the bandgap of the resulting conducting polymer.

The design of low bandgap (E_g) conjugated polymers is presently a very competitive field and remains a major challenge for synthetic chemists. Since E_g governs the intrinsic electronic and optical properties of conjugated polymers, it constitutes the key of many fundamental and technological problems and, in the longer term, of the possible achievement of intrinsic metallic conductivity.

A first approach, extensively investigated in the case of poly(thiophene) (PT),[1] involves the tailoring of the monomer structure in order to increase the quinonoid character of the resulting π-conjugated system at the expense of its aromaticity.[2] This has been achieved by annelation of a benzenic ring to the thiophene nucleus,[3] or by introduction of electron-deficient groups at selected positions of bithiophene.[4]

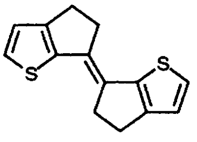
From the observation that interannular rotations around single bonds severely limits the extension of effective conjugation in thiophene oligomers,[5] we have recently shown that an alternative strategy involving the rigidification of the PT π-conjugated backbone by the bridging of the thiophene rings allows a considerable reduction of the bandgap of various thiophene oligomers.[6] On the other hand, previous works have shown that poly(thienylenevinylene) (PTV) has a smaller bandgap than PT.[7] This can be attributed to the presence of double bonds of defined conformations which reduces the aromatic character of the π-conjugated backbone while limiting the number of possible rotations and hence the long-range deviation from planarity In this context, a further rigidification of the π-conjugated system by the bridging of the double bond and thiophene ring could be expected to produce a further reduction of E_g.

In order to test this hypothesis, a first example of rigidified (dithienylethylene) **1**, *i.e.* a simplified model of (PTV) has been synthesized and used as substrate for electropolymerization.

A comparative analysis of the electrochemical and optical properties of the resulting conducting polymer with those of the polymer obtained from dithienylethylene **2** shows that the rigidification leads to considerable changes in the optical and electrochemical properties of the π-conjugated system and to a significant decrease of E_g.

The synthesis of **1** is depicted in Scheme 1. 3-Thienyl propionic acid **5**, obtained by reduction of 3-thienyl acrylic acid **6** with Na/Hg amalgam, was converted into the corresponding acyl choride **4**. Friedel–Crafts acylation afforded the cyclic ketone **3**[8] in 80% overall yield based on **6**. The target compound **1** was then obtained in 70% yield[†] by MacMurry dimerization of **3**.[9]

A single scan voltammogram recorded in a MeCN solution of **1** shows a sharp oxidation peak at 0.72 V followed by two shoulders at 1.16 and 1.50 V.[‡] Comparison of these values with those obtained for **2**, *i.e.* 1.10, 1.40 and 1.66 V



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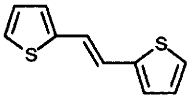

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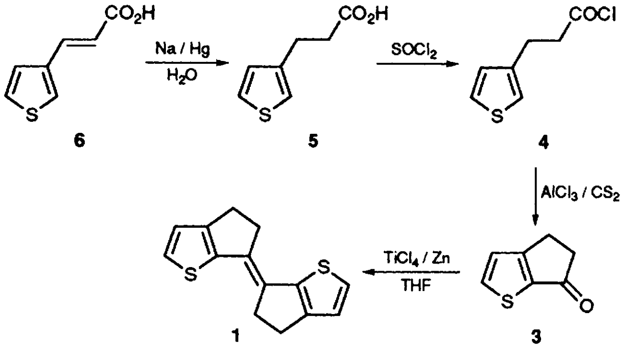

Scheme 1 Synthesis of **1**

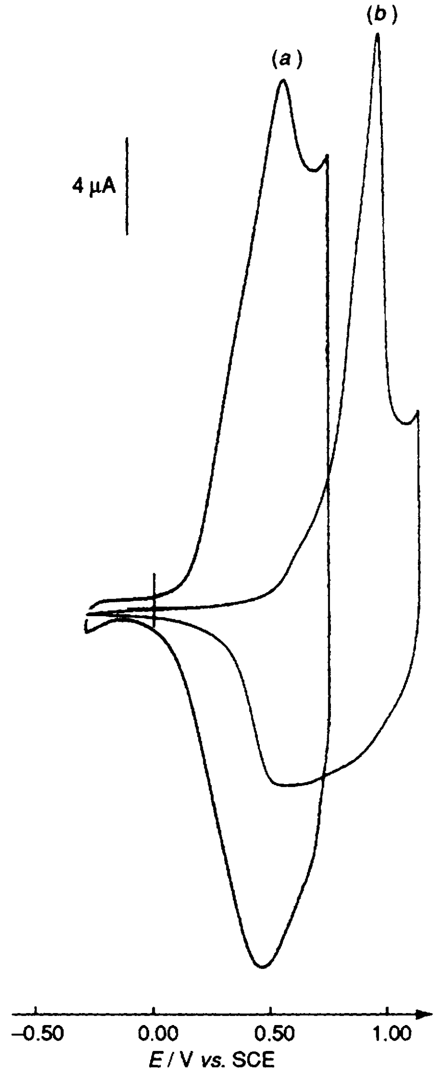

Fig. 1 Cyclic voltammogram of (*a*) poly(**1**) and (*b*) poly(**2**) in 0.1 mol dm^{-3} n-Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}

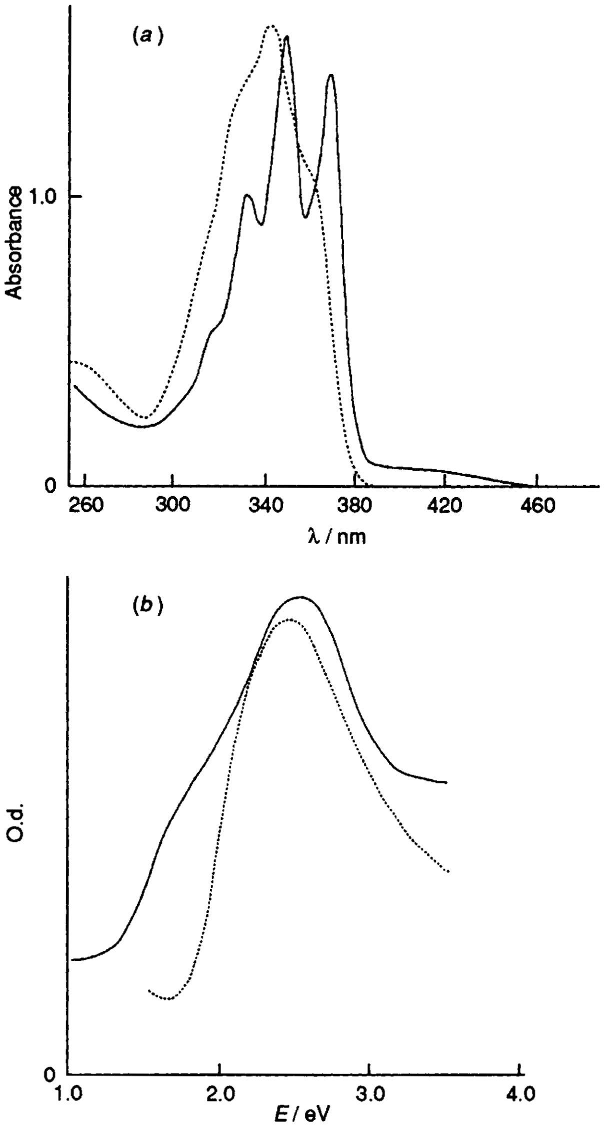

Fig. 2 (*a*) Electronic absorption spectra of **1** (solid line) and **2** (dotted line) in CH_2Cl_2. (*b*) Electronic absorption spectra of neutral films of poly(**1**) (solid line) and poly(**2**) (dotted line) on ITO.

respectively strongly suggests that the effective conjugation is more extended in **1**.

As could be expected, rigidification produces a dramatic loss of the solubility of **1** which falls to 10^{-3} mol dm^{-3}. Despite this low solubility, electropolymerization of **1** by repetitive potential scans occurred steadily and under the same conditions,§ appeared faster than that of **2** as judged by the *ca.* twice larger current peaks corresponding to the redox processes of the polymers in the electrodeposition CVs. Comparison of the CVs of the two polymers (Fig. 1) clearly shows that rigidification induces a large negative shift of the anodic peak potential from 0.98 to 0.58 V and a considerable increase of the symmetry of the CV waves, indicative of an improved electrochemical reversibility.

The electronic absorption spectrum of **2** [Fig. 2(*a*)] shows a shoulder around 330 nm followed by a maximum at 341 nm and a shoulder at 360 nm. As could be expected, the spectrum of **1** exhibits a considerably better resolved fine structure, typical of rigid conjugated systems,[10] while the three maxima shifted to 336, 356 and 367 nm respectively. This bathochromic shift and the emergence of an additional weak absorption band extending to 460 nm appear consistent with the enhancement of effective conjugation indicated by the low oxidation potential. Fig. 2(*b*) shows the absorption spectra of neutral polymer films electrodeposited on optically transparent indium–tin oxide coated glass electrodes. In agreement with previous results, the spectrum of poly(**2**) shows a λ_{max} at 500 nm, while the low energy absorption edge leads to an estimated bandgap of *ca.* 1.80 eV.[11] Comparison of this spectrum with that of poly(**1**) shows that although rigidification does not affect the position of λ_{max}, an additional shoulder strongly reminescent of that already observed for other low bandgap rigidified systems[6] appears on the low energy side of the spectrum. Consequently the low energy absorption onset shifts bathochromically leading to a decrease of E_g to *ca.* 1.40 eV. Larger scale electropolymerization of **1** produced very homogeneous dark blue films. However the films were very stiff and brittle presumably as a result of the rigidified polymer structure. Two-probe conductivity measurements gave values in the range of 10^{-2} S cm^{-1} in agreement with previous results on poly(**2**).[11] However, taking into account the presence of fractures in the films and the fact that two-probe measurements generally give much lower values than the four-probe technique, higher conductivity may be expected from an optimization of electropolymerization conditions.

To summarize we have shown that rigidification of dithienylethylene allows a considerable improvement of the electrochemical reversibility of the resulting conducting polymer and a significant reduction of the bandgap. These promising results suggest that extension of the rigidification approach to longer oligomers of to PTV itself, by the suppression of the remaining possible rotations may lead to a considerable decrease of E_g. Work in this direction is now in progress in our laboratory.

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Footnotes

† Orange powder, mp 205 °C, *m/z* 244 (M^+); ^1H NMR δ 3.0 (m, 4H), 3.27 (m, 4H), 6.92 (d, 2H, *J* = 4.93 Hz), 7.32 (d, 2H, *J* = 4.93 Hz).

‡ 10^{-3} mol dm^{-3} **1** in 0.1 mol dm^{-3} n-Bu_4NPF_6–MeCN, Pt anode of area 7.85 × 10^{-3} cm^2, Pt wire counter-electrode, scan rate 100 mV s^{-1}. All potentials refer to the saturated calomel reference electrode (SCE).

§ 10^{-3} mol dm^{-3} substrate in 0.1 mol dm^{-3} n-Bu_4NPF_6–MeCN, scan rate 100 mV s^{-1}, potential limits: −0.30 to +0.72 V for **1** and −0.30 to +1.10 V for **2**.

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