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A new low band gap dithienylene-fluorovinylene electrochromic polymer: an intriguing effect of silyl substitution on the polymerisation reaction

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Trimethylsilyl substitution at the α position has been claimed to favour both the chemical and electrochemical polymerisation processes of polythiophenes. When comparing the electro-polymerisation of three related monomers we found that the above is not a general rule: the trimethylsilyl substitution does not always produce the expected results because electronic effects play an intriguing role in directing the reaction. One of the three monomers, 1,2-difluoro-1,2-bis(4-methoxy-2-thienyl)ethene, easily underwent electropolymerisation giving a new low band gap polymer with good electrochromic properties.

Introduction

Polythiophenes are widely used materials because of their stability and processability combined with their good electrical and optical characteristics. In particular, they can be successfully synthesised by oxidative electropolymerisation[1,2] although it is generally accepted that electrochemical polymerisation leads to more cross-linked polymers than other chemical methods.[3] Regioselective coupling and highly conjugated polythiophenes have been obtained by introducing trimethylsilyl (TMS) substituents[4–11] at different positions on the thiophene. The relative stabilisation of a carbocation β to a silyl substituent is widely known in organic chemistry.[12] It has been hypothesised that, in the polymerisation reaction, TMS substitution lowers the oxidation potential of the monomer and stabilises the dimeric dication intermediate through hyperconjugative interaction between the electron deficient π molecular orbital of the thiophene ring and the filled σ molecular orbital of the Si–C bond.[8] According to the literature, electronic effects do not seem to play an important role in influencing the polymerisation process even though we have found a few reports on the polymerisation of TMS substituted thiophenes bearing electron-donor[8] or electron-withdrawing groups.[10–11] The objective of this work has been to shed further light on the prospects of using silyl derivatives of thiophene monomers in the electrochemical preparation of conjugated polymers. In particular we considered the possibility of obtaining by this approach polymers from monomers bearing strong electron-withdrawing groups and/or polymers with sequential electron-withdrawing and electron-donor groups. The former polymers, with high redox potentials, are very important for supercapacitor modelling[13] and, when blended with electron-donor polymers, for photovoltaic research,[14–17] while the latter ones are usually low band-gap polymers. To this end, an investigation into the electrochemical polymerisation of the units sketched in Fig. 1 has been undertaken. The monomers used were: (*E*)-1,2-difluoro-1,2-di-2-thienylethene (**DT**); (*E*)-1,2-difluoro-1,2-bis(5-trimethylsilyl-2-thienyl)ethene (**DTS**) and (*E*)-1,2-difluoro-1,2-bis(4-methoxy-5-trimethylsilyl-2-thienyl)ethene (**DTSMO**). In DTSMO alkoxy groups were put in positions 4 and 4′ in order to further stabilise the radical cation produced in the polymerisation process and intensify the effect of TMS groups, thus favouring the coupling between monomer units.

Experimental

Monomers and reagents

The three monomers reported in Fig. 1 (DT, DTS, DTSMO) were prepared by a modification of the Dixon reaction reported

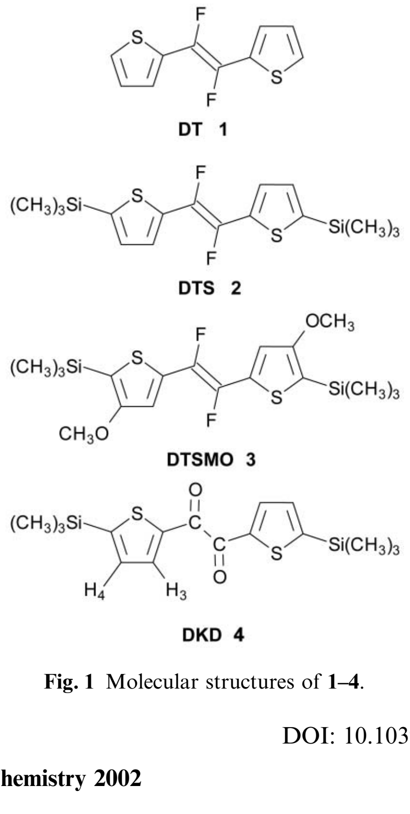

Fig. 1 Molecular structures of **1–4**.

in the literature,[18–20] by reacting lithium derivatives of thiophene with tetrafluoroethene in diethyl ether at −40 °C. Further details on the synthesis and the X-ray structure of DTSMO are given elsewhere.[21] The spectroscopic characterisation of the monomers (^1H, ^{13}C and ^{19}F NMR; chemical shifts are given in ppm, J values in Hz) are reported below.

(*E*)-1,2-Difluoro-1,2-di-2-thienylethene (DT). δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 7.13 (2H, dd, $J_{4,3}$ 3.7, $J_{4,5}$ 4.9, Th(4)-H), 7.40 (2H, dd, $J_{3,4}$ 3.8, $J_{3,5}$ 1.2, Th(3)-H), 7.45 (2H, dd, $J_{5,3}$ 1.2, $J_{5,4}$ 5.1, Th(5)-H). δ_H (500 MHz; $CDCl_3$) 7.13 (2H, m, $J_{4,3}$ 3.7, $J_{4,5}$ 4.9, $J_{4,F}$ 1.7, Th(4)-H), 7.40 (2H, dd, $J_{3,4}$ 3.8, $J_{3,5}$ 1.2, Th(3)-H), 7.45 (2H, m, $J_{5,3}$ 1.2, $J_{5,4}$ 5.1, $J_{5,F}$ 1.7, Th(5)-H). δ_F (500 MHz; $CDCl_3$) −148.4 (m, $J_{F,H}$ 1.7). δ_C (250 MHz; $CDCl_3$; ^1H decoupling) 125.8 (2C, t, J_{CF1} 3.7, J_{CF2} 3.7), 127.8 (2C, t, J_{CF1} 3.7, J_{CF2} 3.7), 128.0 (2C, s), 131.7 (2C, t, J_{CF1} 9.25, J_{CF2} 9.25), 144.7 (2C, dd, J_{CF1} 275.5, J_{CF2} 92.6, =CF).

(*E*)-1,2-Difluoro-1,2-bis(5-trimethylsilyl-2-thienyl)ethene (DTS). δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 0.36 (18H, s, -$SiMe_3$) 7.23 (2H, d, $J_{4,3}$ 3.7, Th(4)-H), 7.44 (2H, d, $J_{3,4}$ 3.7, Th(3)-H). δ_H (500 MHz; $CDCl_3$) 0.36 (18H, br s, -$SiMe_3$) 7.23 (2H, m, $J_{4,3}$ 3.7, $J_{4,F}$ 1.8, Th(4)-H), 7.44 (2H, d, $J_{3,4}$ 3.7, Th(3)-H). δ_F (500 MHz; $CDCl_3$) −145.1 (2F, m, $J_{F,H}$ 1.8, $J_{F,SiMe3}$ 0.5). δ_C (250 MHz; $CDCl_3$) 0.46 (6C, s, Th(5)$SiMe_3$), 127.0 (2C, t, $J_{C,F1}$ 3.7, $J_{C,F2}$ 3.7), 134.8 (2C, s), 136.6 (2C, t, $J_{C,F1}$ 9.2, $J_{C,F2}$ 9.2), 143.4 (2C, t, $J_{C,F1}$ 3.7, $J_{C,F2}$ 3.7), 144.7 (2C, dd, $J_{C,F1}$ 275.5, $J_{C,F2}$ 92.5, =CF).

(*E*)-1,2-Difluoro-1,2-bis(4-methoxy-5-trimethylsilyl-2-thienyl)ethene (DTSMO). δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 0.32 (18H, s, -$SiMe_3$), 3.85 (6H, s, -OMe), 7.16 (2H, s, Th(3)-H). δ_H (500 MHz; $CDCl_3$) 0.32 (18H, s, -$SiMe_3$), 3.85 (6H, s, -OMe), 7.16 (2H, s, Th(3)-H). δ_F (500 MHz; $CDCl_3$) −147.6 (2F, s). δ_C (400 MHz; $CDCl_3$) 0.57 (6C, s, Th(5)$SiMe_3$), 71.8 (2C, s, OMe), 115.0 (2C, t, $J_{C,F1}$ 4.8, $J_{C,F2}$ 4.8), 117.8 (2C, s), 134.6 (2C, t, $J_{C,F1}$ 9.6, $J_{C,F2}$ 9.6), 144.8 (2C, dd, $J_{C,F1}$ 274.6, $J_{C,F2}$ 91.4, =CF), 163.9 (2C, s).

Acetonitrile (AN, UVASOL Merck product) was stored and manipulated under argon pressure; dichloromethane (DM, Merck product *pro analysis*) was dehydrated with $CaCl_2$ for 12 hours, and subsequently distilled in the presence of P_2O_5 under argon and then stored in the dark under argon pressure. Tetrabutylammonium perchlorate (TBAP, Fluka AG "purum") was crystallised from methanol; tetrabutylammonium tetrafluoroborate (TBAFB, Fluka "puriss") was used as received.

Polymerisation details and apparatus

Polymerisation of monomer 1 (DT). Films of poly-DT on indium tin oxide (ITO) plate (Balzers, 23 Ω per □) were synthesised by square wave voltammetry (SWV) of 10 mM DT in AN–DM (1 : 1) + 0.1 M TBAP at 35 °C; the potential was switched between 1.4 V (for 10 s) and −0.5 V (for 10 s) 18 times. By this procedure, which we found to be the best among many others tested, 120 nm thick films, which were not very adherent to ITO, were obtained.

Polymerisation of monomer 2 (DTS). DTS oxidation, carried out in AN + 0.2 M TBAFB, did not result in a polymer but in compound **4** (DKD, Fig. 1). The product was recovered from the electrolysis solution by evaporating the solvent and by extracting the organic fraction with diethyl ether. After ether evaporation the residue was characterised by ^1H and ^{13}C NMR, IR and mass spectrometry. The results reported below are congruent with the proposed chemical structure.

δ_H ($CDCl_3$) 0.38 (18H, s, CH_3), 7.31 (d, J = 3.7, H_4), 8.06 (d, J = 3.7, H_3). δ_C ($CDCl_3$) −0.429 (CH_3), 135.0 (C_4), 137.6 (C_3), 142.8 (C_5), 155.5 (C_2), 182.6 (C=O). IR (film on KBr): the two most intense peaks are at 842 cm^{-1} (CH_3 rocking and Si–C stretching) and 1648 cm^{-1} (C=O stretching). m/z 366 (parent peak), 183 (100%) (half molecule).

Polymerisation of monomer 3 (DTSMO). Films (thickness: 140 nm) of poly-DTSMO were deposited on ITO by cyclic voltammetry (CV) of 3 mM DTSMO solution in AN + 0.1 M TBAP.

Apparatus. An AMEL 5000 multifunction apparatus was used for electrosynthesis and electrochemical characterisation. For all electrochemical experiments a Pt wire was used as the counter-electrode and a saturated calomel electrode (SCE) was used as reference; both electrodes were separated from the electrosynthesis solution by a glassy septum. Cyclic voltammetries of polymer films were carried out in pure AN + 0.1 M TBAP.

Optical spectra of films were obtained on a Perkin-Elmer LAMBDA9 spectrophotometer and their thickness measured by a Tencor profilometer (Alpha Step 200). X-Ray diffraction patterns on polymer films were recorded at room temperature by a Philips powder diffractometer (PW1050/81-PW1710). Cu-Kα X-radiation (wavelength 1.5418 Å) was used and the step scanning recording was performed in the 2θ range of 3–50° .

Results and discussion

Electropolymerisation of (*E*)-1,2-difluoro-1,2-di-2-thienylethene (DT)

As reported in the Experimental section, we could not obtain films of poly-DT by CV but only by SWV. Fig. 2(a) shows the absorption spectrum of one of these films, which displays a maximum absorbance at about 400 nm. This value is very low and, if compared with that of the starting monomer (332 nm),

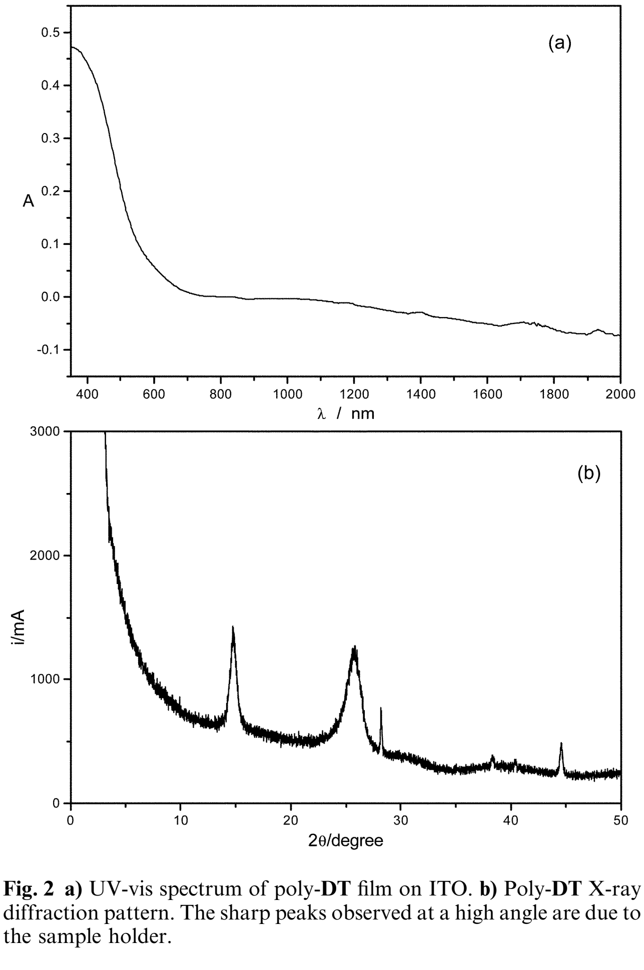

Fig. 2 a) UV-vis spectrum of poly-**DT** film on ITO. **b)** Poly-**DT** X-ray diffraction pattern. The sharp peaks observed at a high angle are due to the sample holder.

suggests the presence of only oligomeric products probably derived from a single coupling reaction. This behaviour is in agreement with that reported in the literature for the electrosynthesis of thiophene monomers bearing electron-withdrawing groups.[1] The DT monomer has been studied previously and gave comparable results.[22] The oligomeric nature of electrosynthesised poly-DT is also confirmed by the sharpness of the peaks in the X-ray diffraction pattern (Fig. 2(b)).[23]

Electropolymerisation of (*E*)-1,2-difluoro-1,2-bis(5-trimethylsilyl-2-thienyl)ethene (DTS)

A trimethylsilyl group was then introduced into monomer **1** in order to lower the oxidation potential, as has been reported for thiophene and bithiophene,[11] as well as to increase the molecular weight of the polymer obtained by as much as 14–64 times that obtained by the electropolymerisation of the corresponding non-silylated monomers.[8] The polymerisation of the new monomer DTS has been attempted at several temperatures (from 20 to 45 °C) with monomer concentrations up to 5 mM in AN + 0.2 M TBAFB. According to a suggestion from the literature,[5,8] the electrolyte was changed from TBAP to TBAFB in order to favour the elimination of the trimethylsilyl cation as Me_3SiF. Changing the solvent from AN to DM had no effect on the results. The cyclic voltammogram of one of these solutions is shown in Fig. 3(a). The DTS voltammetric peak was not meaningfully shifted towards less positive potentials compared with the corresponding peak of DT, revealing that the polymerisation of DTS is not energetically favoured, unlike the case of 2,5-bis(trimethylsilyl)-3-bromothiophene compared with 3-bromothiophene.[10] Neither by CV nor by potentiostatic oxidation was it possible to deposit any poly-DTS film on the electrode.

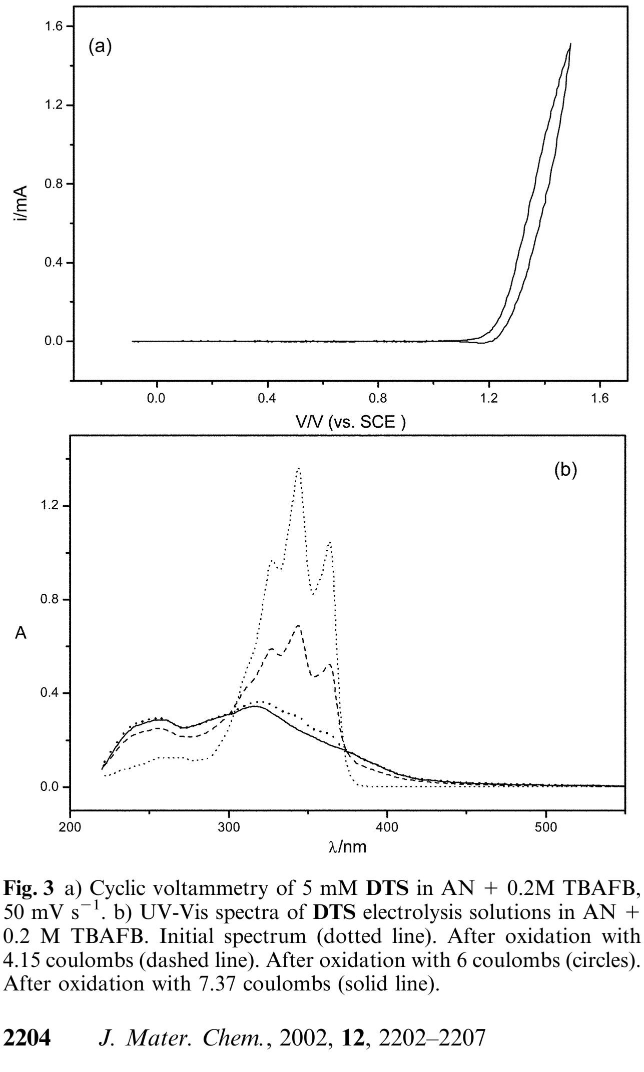

Fig. 3 a) Cyclic voltammetry of 5 mM **DTS** in AN + 0.2M TBAFB, 50 mV s^{-1}. b) UV-Vis spectra of **DTS** electrolysis solutions in AN + 0.2 M TBAFB. Initial spectrum (dotted line). After oxidation with 4.15 coulombs (dashed line). After oxidation with 6 coulombs (circles). After oxidation with 7.37 coulombs (solid line).

In order to analyse the products of DTS oxidation, 5 mM solutions were electrolysed at 1.5 V (a potential close to that of the oxidation peak, see Fig. 3(a)) in AN with 0.2 M TBAP and 0.2 M TBAFB. In both cases, after a flow of about 1 faraday mol^{-1}, a very low current was reached. UV-Vis spectra before, during and after electrolysis of one of these solutions are shown in Fig. 3(b). There was no evidence that polymerisation had occurred, but the compound DKD (Fig. 1) was recovered in high yield from the reaction medium (see Experimental section). In conclusion, oxidation is localised on the carbon atoms of the ethene double bond. As a crude hypothesis, arising from experimental evidence gathered so far, this suggests that the electron-withdrawing fluorine induces a partial positive charge on the adjacent carbon atoms. Therefore the radical cation is mainly localised on the ethene double bond preventing homolytic or heterolytic detachment of the trimethylsilyl groups. Consequently, the reactions of the radical cation with traces of water contained in the solvent take place at the ethene double bond, causing fluorine to be substituted by an OH^- group followed by proton elimination.

Electropolymerisation of (*E*)-1,2-difluoro-1,2-bis(4-methoxy-5-trimethylsilyl-2-thienyl)ethene (DTSMO)

Following the failure of the polymerisation of DTS we therefore decided to introduce an alkoxy substituent into the thiophene ring (monomer **3**, DTSMO) to further stabilise the carbocation in position 4. This modification dramatically changed the electrochemical behaviour in favour of the polymerisation process. Fig. 4(a) illustrates the polymerisation by CV of 3 mM DTSMO in AN + 0.1 M TBAP; by this method a very adherent polymer film grew on the ITO electrode. The polymer was highly conjugated, as demonstrated by the absorbance spectrum (maximum wavelength = ~600 nm,

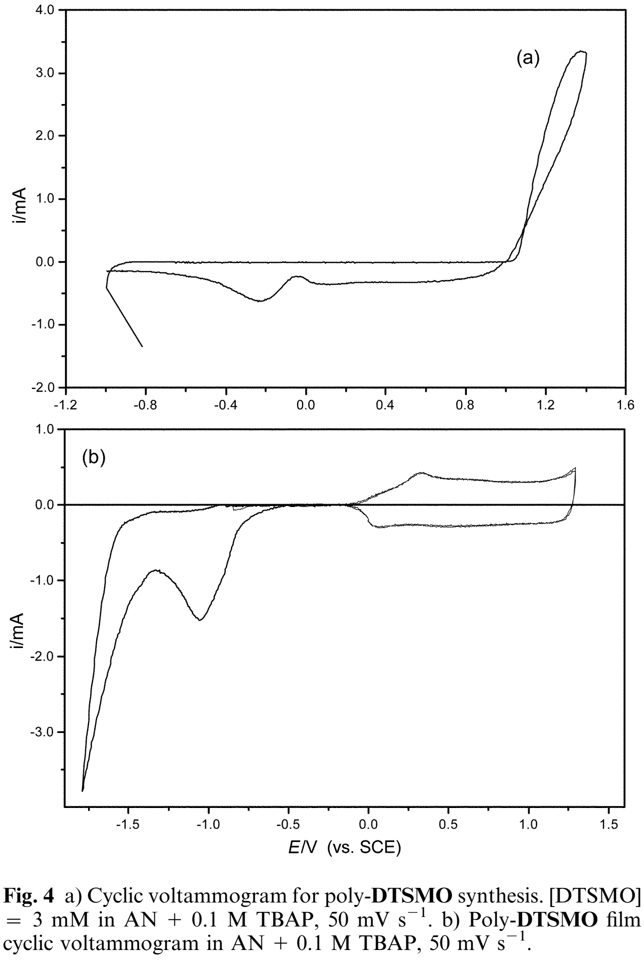

Fig. 4 a) Cyclic voltammogram for poly-**DTSMO** synthesis. [DTSMO] = 3 mM in AN + 0.1 M TBAP, 50 mV s^{-1}. b) Poly-**DTSMO** film cyclic voltammogram in AN + 0.1 M TBAP, 50 mV s^{-1}.

see Fig. 7(a)). This indicates that the coupling reaction occurs easily. During the polymerisation, the percentage of reduction (cyclable) charge *vs.* the total anodic charge, calculated from the preparative CV curves, was abnormally high at 40%. On the other hand, from the CV of the grown polymer (Fig. 4(b)), assuming a polymer density equal to 1, we calculated about 0.5 cyclable charges per monomer unit (0.25 per thiophene moiety), in very good agreement with the results obtained for poly(dithienylene-vinylene)[24] and for most polythiophenes. In an electrochemical polymerisation following the usual pathway, 0.5 charge per monomer unit would correspond to a ratio of 20% of cathodic to anodic charge in preparative CV. The very high ratio (40%) found for our polymer leads to the hypothesis that the polymerisation mechanism is different from that usually proposed. Both the coupling reaction and the trimethylsilyl elimination mechanisms should therefore be revised. One possible hypothesis is that the neutral monomer (M), favoured by the presence of the electron-releasing alkoxy group, nucleophilically attacks the generated radical cation (CR), giving the intermediate shown in Fig. 5. In thiophene polymerisation such a CR–M coupling (mechanism A reported below)[25,26] was proposed as an alternative to the more widely accepted CR–CR dimerisation mechanism (mechanism B).[26] In both mechanisms the proton or the trimethylsilyl cation are eliminated to give the neutral molecule. In our case we have to consider one of the two trimethylsilyl groups eliminated to be a radical, thus conserving a considerable amount of charge (mechanism C).

$$\mathrm{M}^{\bullet+} + \mathrm{M} \rightarrow \mathrm{D}^{\bullet+} \text{ (mechanism A)}$$

$$\mathrm{D}^{\bullet+} + \mathrm{M}^{\bullet+} \rightarrow \mathrm{D} + \mathrm{M} + 2\mathrm{Me_3Si}^{+}$$

$$\mathrm{M}^{\bullet+} + \mathrm{M}^{\bullet+} \rightarrow \mathrm{D} + 2\mathrm{Me_3Si}^{+} \text{ (mechanism B)}$$

$$\mathrm{M}^{\bullet+} + \mathrm{M} \rightarrow \mathrm{D} + \mathrm{Me_3Si}^{+} + \mathrm{Me_3Si}^{\bullet} \text{ (mechanism C)}$$

Of course such coupling steps could also occur between oligomers that are longer than that shown in Fig. 5. Since the proposed mechanism is a rough, though reasonable, hypothesis, further investigation is required in order to shed light on this subject.

Poly-DTSMO characterisations

The CV of poly-DTSMO (Fig. 4(b)) shows the doping oxidation process in the ∼0.1–1.0 V range. Moving towards negative potentials, a first reduction peak at −1.06 V was observed and attributed to the irreversible loss of fluoride followed by proton addition; a second irreversible reduction peak, inherent in the reduction of the new π-conjugated system, occurred at −1.5 V. This potential is in accord with that of a thienylene-vinylene polymer (without fluorine) and this assumption is confirmed by the successive oxidation that occurs at a higher potential.[22]

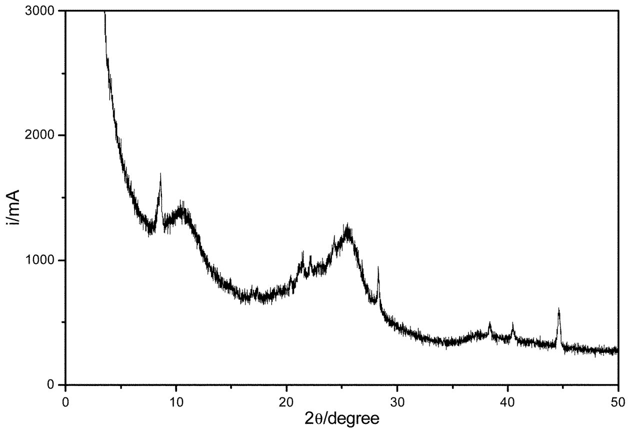

Fig. 6 Poly-**DTSMO** X-ray diffraction pattern. The sharp peaks at low angles are due to TBAP while those at high angles are due to the sample holder.

The X-ray diffraction pattern suggests that poly-DTSMO films have some degree of supramolecular order (Fig. 6). Besides the peaks due to the polymer, small and sharp peaks due to the electrolyte and to the sample holder are also visible. Very few X-ray diffraction spectra of poly(thienylene-vinylenes) have been reported and all are alkyl derivatives[27] even though several alkoxy-substituted polymers of this family have been prepared, such as poly[bis(3,4-ethylenedioxy-2-thienylene)-vinylene][28,29] and poly(3,4-dibutoxy-2-thienylene-vinylene).[30–32] The main features of the spectra reported in the literature[27] are the presence of a relevant amorphous part in the polymer and the presence of a small angle diffraction peak that shifts as a function of side-chain length as in poly(alkylthiophenes). Following from this the interchain distance, evaluated from our spectrum, is about 8.5 Å, a value considerably shorter than that reported for 3,4-dibutylthiophene-2,5-diylvinylene (13 Å), giving an indication of tightly self-assembled polymer chains. Obviously, a dibutyl derivatives does not represent a good reference model because of the steric hindrance of the double alkyl substitution in the thiophene unit; moreover, it is well known that in thiophene polymers alkoxy groups are less sterically demanding than alkyl groups.[33]

The band gap evaluated from the UV-vis absorption spectrum (Fig. 7(a)) was 1.42 eV confirming the effectiveness of the alternation of donor–acceptor substituents in lowering the polymer band gap.[34] This value is consistently lower than

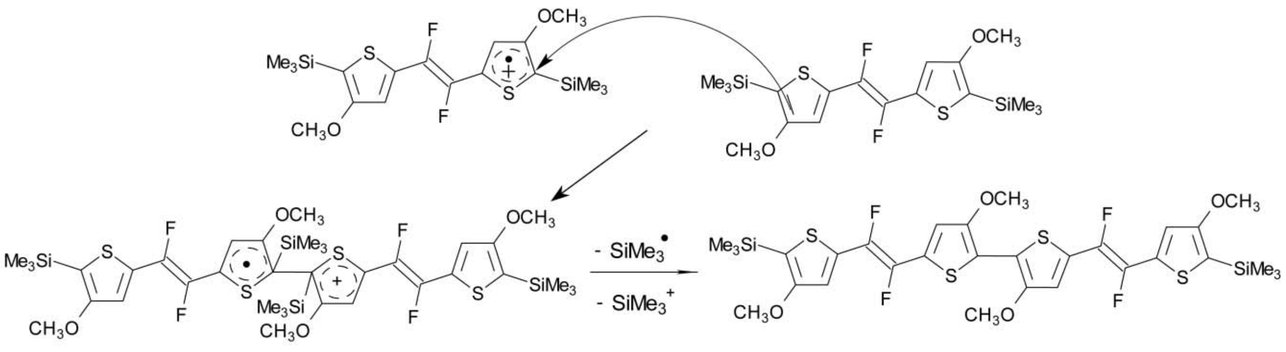

Fig. 5 Mechanism for the electropolymerisation of Poly-**DTSMO**.

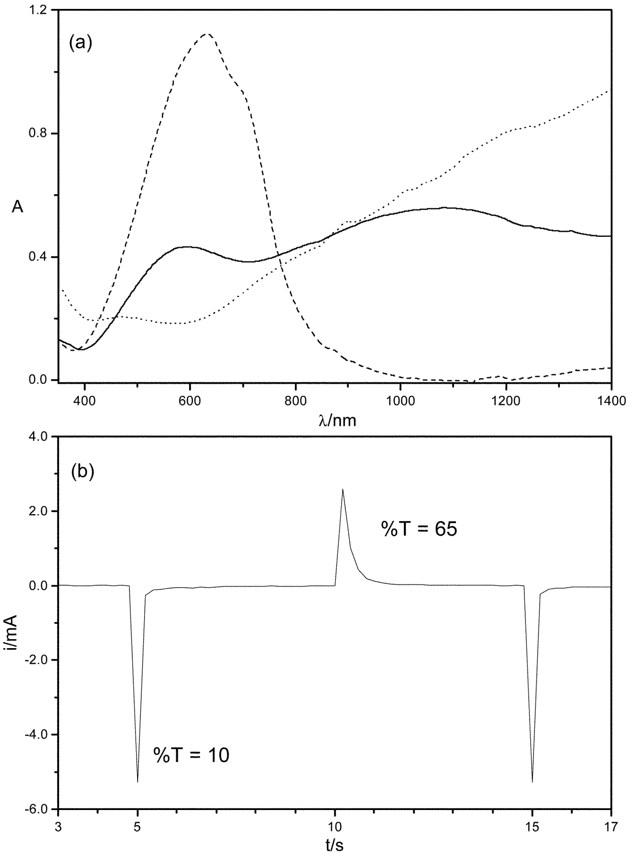

Fig. 7 a) UV-vis spectra of Poly-**DTSMO** film on ITO at three levels of doping (potentials *vs.* SCE): −0.1 V (dotted line); +0.6 V (solid line); +1.3 V (dashed line). b) Poly-**DTSMO** film potential square wave in AN + 0.2 M TBAP: −1 V for 5 s, +0.4 V for 5 s.

those reported for poly(methoxythienylene-vinylene) (1.55 eV)[35] and poly(dibutoxythienylene-vinylene) (1.62–1.69 eV)[30,31] and of the same order of magnitude of poly[bis(3,4-ethylenedioxy-2-thienyl)vinylene][28,29] (1.48–1.4 eV) where a strong donating effect of the ethylenedioxy bridge is present.

Electrochromic properties of poly-DTSMO

The films prepared on transparent supports by electro-oxidation were adherent and compact, and showed remarkable electrochromic properties. The current yield of polymer preparation by CV was very high (approximately twice that of most polythiophenes). As Fig. 7(a) illustrates, the absorbance spectrum of the neutral form covers almost the entire visible range, while the fully oxidised form transmits up to 80% of the visible light. A favourable peculiarity of the poly-DTSMO electrochromism is the very fast doping–dedoping kinetics, as shown in Fig. 7(b). A high resistance to repetitive electrochromic cycles was ascertained and makes this polymer a good candidate for application in solid state electrochromic devices.

Conclusions

The results of this investigation has led to some important conclusions.

1. The DT monomer behaves in the usual way in the polymerisation process, even if only oligomeric products are obtained. The introduction of a trimethylsilyl group completely changed the reactivity of the molecule and no traces of oligomers or polymer were found. Only the diketo molecule **4** (DKD) was recovered from the reaction medium.

2. It can be hypothesised that even if, in the initial oxidation step the radical-cation is generated on the thiophene ring, it then moves onto the ethylene bond. This favours nucleophilic substitution of the fluorine by OH^- groups (probably from the solvent) followed by rearrangement of the molecule and elimination of the hydrogen cation.

3. The introduction of an alkoxy group dramatically changed the monomer reactivity, favouring the coupling between thiophene moieties. The cleavage of the C–Si bond occurred easily and gave rise to highly conjugated polymer films, but the current yield was abnormally high, suggesting a mechanism partially involving neutral radicals. Additional work is needed in order to completely clarify the polymerisation mechanism.

4. Very adherent and compact films can be prepared by electrochemical polymerisation of DTSMO. The resulting polymer presents a low band gap and has very interesting electrochromic features, such as very fast doping–dedoping kinetics and a steep colour variation from blue to transparent during the transition from the neutral to the oxidised form.

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