Reduction of the Steric Hindrance to Conjugation in 3,4-Disubstituted Poly(thiophenes); Cyclopenta[*c*]thiophene and Thieno[*c*]thiophene as Precursors of Electrogenerated Conducting Polymers

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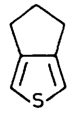
The cyclopenta[*c*]thiophene (**1**) and thieno[*c*]thiophene (**2**) have been synthesized and used as substrates for electropolymerization; steric hindrance is less in poly(**1**) than in poly(3,4-dialkylthiophenes), while attempts to electropolymerize (**2**) were unsuccessful.

The design of new organic conducting polymers is at present a very active field of research. Among the many compounds that have been investigated poly(thiophene) derivatives have received increasing attention because of their good chemical stability and the advantages of their electrochemical synthesis.[1] It has been shown that the introduction of a methyl group at position 3 leads to a considerable enhancement of the conductivity. This effect has been attributed to a statistical decrease of the number of parasitic 2–4′ couplings that interrupt the conjugation along the polymeric chains and also to the inductive effect of the methyl group, which lowers the oxidation potential of the monomer and thus leads to a less reactive radical cation during the electropolymerization.[2] The use of 3,4-dialkylthiophene monomers could be an interesting way to synthesize more stereoregular polymers by preventing any possibility of 2–4′ coupling. However, as shown in previous work, this approach is drastically limited by the steric hindrance to planarity of the conjugated system in the corresponding polymers.[3] The torsion angle between adjacent 3,4-disubstituted-thiophene units leads in these cases to an important loss of conjugation. In an attempt to reduce this steric interaction, dihydro-cyclopenta[*c*]thiophene (**1**) and -thieno[*c*]thiophene (**2**) have been synthesized and we report here the results of their electropolymerization.

The cyclopenta[*c*]thiophene (**1**) was synthesized using a method derived from that described by MacDowell *et al.*[4] The electropolymerizations were performed in a one compartment three-electrode cell containing 0.2 M monomer and 0.02 M Bu_4NPF_6 in nitrobenzene. The solvents and reagents were purified according to the previously described procedures.[5b]



(**1**)

(**2**)

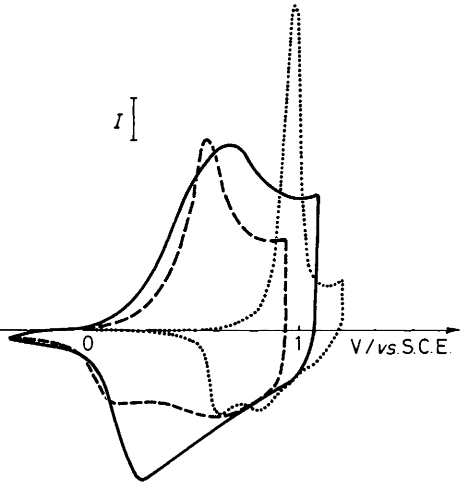


Figure 1. Cyclic voltammograms recorded in 0.1 M $LiClO_4$–MeCN, scan rate 50 mV s^{-1}. (– – –) PMeT, I = 20 µA, deposition charge Q_d = 7 mC; (——) Poly (**1**), I = 20 µA, Q_d = 10 mC; (· · · · ·) PMe_2T, I = 40 µA, Q_d = 7 mC.

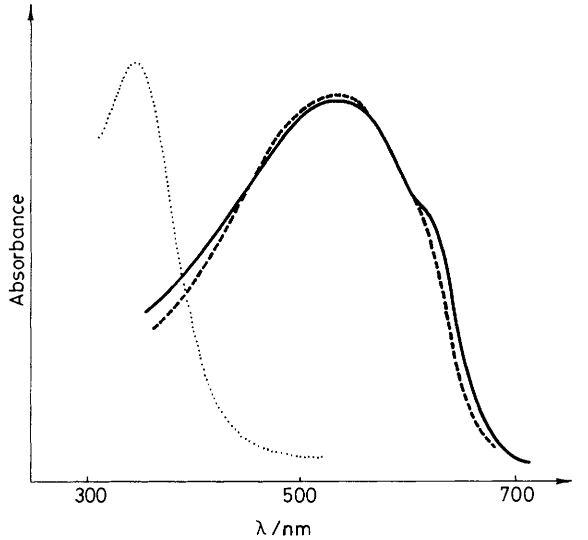


Figure 2. Visible absorption spectra of electrochemically undoped polymers on an indium–tin oxide transparent electrode. (– – –) PMeT; (——) Poly (**1**); (· · · · ·) PMe_2T.

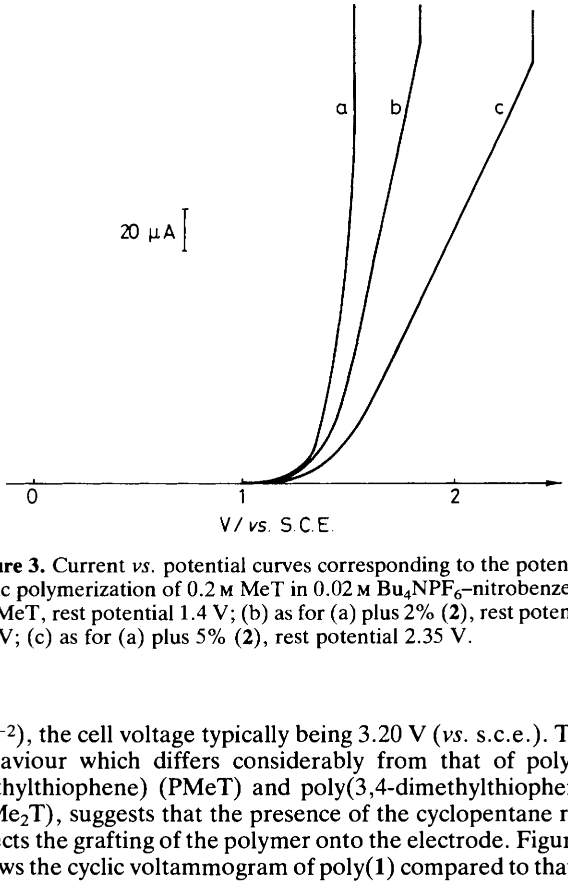


Figure 3. Current *vs.* potential curves corresponding to the potentiostatic polymerization of 0.2 M MeT in 0.02 M Bu_4NPF_6–nitrobenzene. (a) MeT, rest potential 1.4 V; (b) as for (a) plus 2% (**2**), rest potential 1.8 V; (c) as for (a) plus 5% (**2**), rest potential 2.35 V.

The anode was either a platinum disk electrode of 0.07 cm^2 area or an indium–tin oxide transparent electrode; aluminium foil was used as cathode and a saturated calomel electrode (s.c.e.) as reference. In the case of (**1**), a potential sweep in the reaction medium shows that the current increases sharply at 1.30 V. This value is lower than that obtained for 3-methylthiophene (1.40 V), as expected from the presence of two electron-donating substituents on positions 3 and 4. When the potential is held at this value, the current increases for only a few seconds then decreases, while large quantities of coloured soluble products appear near the working electrode. These results suggest that under these conditions the polymerization is self-inhibiting and is limited to short chain oligomers. This conclusion is confirmed by the fact that the charge exchanged upon reduction of the polymer is nearly constant whatever the value of the deposition charge. Homogenous films continuously covering the electrode surface are obtained only when operating with high values of the current density (10 mA cm^{-2}), the cell voltage typically being 3.20 V (*vs.* s.c.e.). This behaviour which differs considerably from that of poly(3-methylthiophene) (PMeT) and poly(3,4-dimethylthiophene) (PMe_2T), suggests that the presence of the cyclopentane ring affects the grafting of the polymer onto the electrode. Figure 1 shows the cyclic voltammogram of poly(**1**) compared to that of PMe_2T and PMeT. The anodic current peak of poly(**1**) occurs at 0.74 V s.c.e. This value is lower than that for PMe_2T (1.00 V) but higher than that for PMeT (0.56 V). These results suggest that the steric hindrance to conjugation is noticeably less than in PMe_2T, but that it is still higher than in PMeT. Figure 2 shows the visible absorption spectra of the undoped polymers. The position of the absorption maximum of PMe_2T (350 nm) confirms the appreciable loss of conjugation in the polymer due to the torsion angle between adjacent monomer units. However, the absorption maximum of poly(**1**) (510 nm) is very close to that of PMeT (520 nm), indicating that the cyclization between positions 3 and 4 considerably reduces the steric hindrance and that the polymer has recovered its planarity. Preliminary conductivity measurements on poly(**1**) films by the two probe technique gave values in the range of 10—20 S cm^{-1}. Although higher than the conductivity of PMe_2T (0.5 S cm^{-1}), these values are much lower than the conductivity of PMeT films (450—500 S cm^{-1}).[5] Since absorption spectra indicate that the mean conjugation length is approximately equivalent in PMeT and poly(**1**), the lower conductivity of poly(**1**) suggests that the cyclopentane ring modifies the inter-chain contacts in the polymer.

The thieno[*c*]thiophene (**2**) was prepared using a synthesis derived from that described by Zwanenburg and Wynberg.[6] Although never previously synthesized, poly(**2**) has already been the object of theoretical studies by Bredas *et al.*, who concluded that owing to the expected stabilization of its quinoid form, this polymer should have a much lower energy gap than the parent poly(thiophene).[7] Two different sets of conditions have been tested for the electropolymerization of (**2**): conditions A, as above, and conditions B, 0.3 M (**2**), 0.05 M Bu_4NClO_4 in nitrobenzene. A potential sweep carried out in these two reaction media shows the presence of a first oxidation wave at 1.20 V *vs.* s.c.e., and a second wave beginning at 1.80 V. The absence of a reduction wave in the reverse scan, whatever the anodic limit of potential, shows that no electropolymerization occurs. This suggests that the sulphide function, which is more easily oxidized than the thiophene ring, could capture the radical cations produced by the oxidation of the thiophene ring. In order to confirm this hypothesis, we analysed the electropolymerization of 3-methylthiophene in the presence of small quantities of (**2**). Figure 3 shows the *I vs.* V curves corresponding to the potentiostatic polymerization of MeT in reaction media (conditions A) containing increasing amounts of (**2**). These curves show clearly that in the presence of 5% of (**2**), the electropolymerization of MeT requires an overpotential of almost 1 V (2.35 instead of 1.40 V), confirming that (**2**) acts as a radical scavenger. Thus it appears that the preparation of poly(**2**) could be achieved more easily by chemical polymerization.

In summary, we have shown that in the case of (**1**), the cyclization between positions 3 and 4 on the thiophene ring causes reduction of the steric hindrance to conjugation in the polymer [*cf.* poly(3,4-dialkylthiophenes)]. However, this enhancement of the conjugation does not lead to the expected improvement in the conductivity. This could be because of modifications in the inter-chain contacts and possible problems related to the grafting of the polymer onto the electrode surface. In (**2**), the presence of the sulphide function renders conventional electropolymerization of the compound difficult.

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