'In situ' spectroelectrochemical study of a series of $\alpha,\alpha'$-dimethyl end-capped oligothiophene films

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Abstract

The electrooxidation of $\alpha,\alpha'$-coupled thiophene oligomers alkyl-protected toward anodic coupling at the terminal $\alpha$ positions was studied in solid state at room temperature. Reversible oxidation goes from a single one-electron step oxidation for the tetramers to two separate one-electron steps for the pentamer and hexamer. The oxidation potentials are found to be primarily dependent on the conjugation length of the oligothiophene chain. The 'in situ' visible spectra of the electrochemically prepared oxidation states have also been investigated. A model based on the formation of charged molecular associates such as $\pi$-dimers or $\pi$-stacks successfully explains the spectroscopic results.

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1. Introduction

After the discovery that polyconjugated organic polymers become electrical conductors upon electrochemical and chemical doping, great attention has been devoted to five-membered aromatic heterocycles, mainly to thiophene- and pyrrole-based polymers. Conducting polymers encompass a wide range of conductivities, from insulator to metallic-like electronic conductivity according to their doping levels [1,2].

Although conducting polymers of a defined composition can now be reproducibly prepared, long-chain polythiophenes have the complexity of the 'real' polymer such as solubility, structural defects, broad distribution of the chain length, etc. Semiconducting oligomers are currently being investigated as good models for studying charge storage in conducting polymers [3–9]. Oligomers are well-defined chemical systems where the conjugation chain length can be exactly controlled. A regular structure of the crystal makes the oligothiophenes good candidates for molecular electronics applications such as field-effect transistors (FETs) [10] or light-emitting diodes (LEDs) [11–14].

Conventional nonsubstituted oligothiophenes suffer from chemical instability because of the high chemical activity on both $\alpha$ carbons of the terminal thiophene rings. The substitution of the two positions has proved very effective in enhancing chemical stability, keeping the resulting compounds very electroactive [15]. The $\alpha,\alpha'$-substitution at the terminal positions also prevents the possibility of further polymerization upon chemical doping and, at the same time, the resulting oxidized species remain stable for a long time [16]. Moreover, the direct investigation of the electrochemical oxidation of thiophene itself remains very difficult due to the high reactivity of the thiophene cation radical and the fast formation of a polymer layer on the electrode surface [17]. In this respect, the study of oligomers in which thiophene units are blocked by their $\alpha$-positions can provide useful information concerning charge storage in polyconjugated materials.

Most redox and spectroelectrochemical studies on conjugated oligothiophenes have been carried out in solution [18–22]. Due to the decrease in solubility with increasing chain length, such investigations of solution properties were limited to very short oligomers. Furthermore, studies in solution cannot consider the solid-state properties of the polymer.

The chemical $I_2$ or $\text{NOBF}_4$ doping of CH$_3$-capped oligothiophenes has been studied by Hotta and Waragai in the solid state [23]. In order to rationalize the near-UV–Vis spectroscopic data, they propose a model based on the formation of molecular aggregates. On the other hand, procedures for the preparation of organic radical salts by applying...
electrochemical oxidation have also been established [24]. Moreover, the electrochemistry and ‘in situ’ ESR of even (from the tetramer to the decamer) dimethyl end-capped oligothienyls in the solid state have been studied [25].

Considering these factors, the present contribution is focused on the controlled electrochemical preparation of solid-state oxidized methyl-protected oligothiophenes. A dependence of the spectroelectrochemical properties on the chain length may be observed within the series. Thin films of α,α′-dimethyl substituted oligothienyls from the tetramer to the hexamer (see Fig. 1) have been employed in the present study. Furthermore, the ethyl-substituted end-capped tetramer (DEQqT) is comparatively studied to evaluate the influence of the chain size on the stability of the charged species.

2. Experimental

The oligomers used in this work are given in Fig. 1. The synthesis and characterization of the α,α′-dimethyl oligothiophenes (from the tetramer to the hexamer) are described elsewhere [15,26,27]. Experiments were performed using acetonitrile (AN) as the solvent, which was supplied by Aldrich in analytical grade. Tetraethylammonium perchlorate (0.1 M, TEAP) was used as the supporting electrolyte. The working electrode used was a platinum sheet of 1 cm² of surface area. The counterelectrode was of steel and the reference electrode was an Ag/AgCl electrode ($E^\circ = 0.222$ V). All values of the potentials were measured at the maximum of the oxidation wave. Films were prepared on the working electrode by deposition of the sample from a 1,2-dichloromethane solution, followed by solvent evaporation.

The experimental procedure was as follows: First, the coated electrode was translated into the 0.1 M TEAP acetonitrile solution where the neutral oligomer is insoluble. Then the coated electrode was submitted to a potential sweep between 0.0 and 1.2 V with a scan rate of 25 mV/s. A PAR 273 potentiostat-galvanostat governed by an Atlas PC compatible microcomputer through M270 software from EG&G was employed to perform the redox state of the oligomers.

Optical measurements were performed using a reflection–absorption system according to the experimental scheme of Fig. 2. The light was guided inside the electrochemical cell by using an optic fiber. A second optic fiber was used to guide the reflected light, from the electrode, to an array diodes system detector [17]. All the spectra were obtained taking as background the absorbance of the coated electrode in the solution before the electrochemical oxidation. The visible spectra of the oxidized molecules were recorded between 500 and 1000 nm, where the oxidized oligothiophene films present important absorptions, simultaneously to the oxidation/reduction of the oligomers during the anodic and cathodic branches of the voltammetric experiment: one spectrum was recorded every 20 ms.

3. Results and discussion

3.1. Cyclic voltammetry

In general, the neutral forms of these oligomers are insoluble at room temperature in the solvent–electrolyte system.
used for this purpose. However, for the shorter oligomers, problems can be found due to the fact that the material, insoluble in its pristine state, can be partially solubilized by oxidation due to the higher solubilities of the oxidized state. Under these conditions (acetonitrile and TEAP) only a partial dissolution of the oligomers can be observed from the electrode during the electrochemical experiment. The cyclic voltamograms of thin films of DMQtT, DMQqT, and DMSxT (see Fig. 1 for chemical nomenclature) in 0.1 M TEAP-AN, in the potential range 0.0–1.2 V, are reported in Fig. 3 and the redox potentials of the different end-capped oligothiophenes investigated are summarized in Table 1.
Table 1
Oxidation peak potentials for films of \( \alpha,\alpha' \)-dialkyl oligothiophenes in 0.1 M TEAP-AN (scan rate 25 mV/s)

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>( E_1 ) (V)</th>
<th>( E_2 ) (V)</th>
<th>( \Delta E ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMQ( \text{T} )</td>
<td>0.941</td>
<td>1.200</td>
<td>0.259</td>
</tr>
<tr>
<td>DMQ( \text{Q} \text{T} )</td>
<td>0.920*</td>
<td>1.057</td>
<td>0.137</td>
</tr>
<tr>
<td>DMSxT</td>
<td>0.910</td>
<td>1.046</td>
<td>0.136</td>
</tr>
<tr>
<td>DEQ( \text{T} )</td>
<td>0.940</td>
<td>1.160</td>
<td>0.220</td>
</tr>
</tbody>
</table>

*Higher potential value between 0.85 and 0.920 V.

The tetramer (Fig. 3(a)) shows a single reversible cycle, \( E = 0.941 \) V, which involves the reversible formation of the radical cation. It also shows a second peak around \( E = 1.200 \) V which, under these experimental conditions, is not reversible. The continuous cycling of the potential promotes a decrease of the current on the consecutive voltammograms due to a partial solubility of the radical cation in this electrolyte [28]. The potential of the experimental maxima on the voltammogram, related to those of Zotti et al. [25], are shifted to more anodic values due to the high compaction of the film, and most important, to the use in both cases of a different electrochemical medium. Nonetheless, the difference between the two oxidation peaks (\( \Delta E \)) for each oligomer is equal to those reported by Zotti. The DMQ\( \text{T} \) and DMSx\( \text{T} \) films show two well-defined reversible waves, thus indicating the generation of species which are stable within the time scale of the voltammetry experiments at least during several cycles. These two reversible waves involve the formation of the cation radical and its further oxidation to the dication [25,28]. By increasing the thickness of the film both peaks overlap giving one unresolved maximum which involves the two oxidation processes.

The oxidation potentials show a decreasing trend from the tetramer to the hexamer. As was observed using other oligomeric systems the oxidation potential of the oligomers decreases when the chain length increases [18,21], both \( E_1 \) and \( E_2 \) scale linearly with \( 1/N \) (see Fig. 4). This fact is due to the increasing conjugation length which favors the \( \pi \)-electronic delocalization and reduces the oxidation potentials. As previously noted for silyl-terminated oligomers [18], \( E_2 \) shifts faster than \( E_1 \) when oligomer length increases. The stability of dications depends on the minimization of the repulsions between the two positive charges, and longer oligomers are more effective in reducing these repulsions.

Voltammograms performed on a solid film of the oligomer exhibit strong hysteresis or relaxation effects [25,29,30]. Upon discharging, all reversal peaks are shifted towards lower energies compared to the corresponding original peaks upon charging. This effect is caused by an energetic impediment to the first oxidation process because the counterions have to break the crystalline structure of the oligomer. Then, they have to induce conformational movements on the chains in order to create a free volume which can be occupied by both counterions and solvent molecules, coming into the crystalline lattice [31]. An amorphous and gel structure is generated.

The second electronic transfer is easier because the diffusion of counterions inside the amorphous gel expends only a low energy, related to the shrinking of the gel. The second oxidation process does not need any breaking of the oligomeric lattice. This relaxation process generates a shift of the oxidation peak to higher potentials (0.920 and 1.057 V for the pentamer or 0.910 and 1.046 V for the hexamer), and to lower potentials during the reduction sweep (0.600 and 0.700 V for the pentamer or 0.670 and 0.720 V for the hexamer), closer to the equilibrium potential.

Our data, when compared with the unsubstituted compounds [32], confirm that the \( \alpha,\alpha' \)-dimethylation and \( \alpha,\alpha' \)-diethylation induce a stabilization of the system due to an effect of electrodonation by the methyl and ethyl groups. On the other hand, an inductive effect of the ethyl group with respect to the methyl group only is observed in the second oxidation peak. In the first oxidation process, the neutral molecule is planarized to a quinoid structure [33] being a more effective overlapping of the \( \pi \)-system; in this structural disposition the electron-donating properties of the substituents become more relevant and \( E_2 \) is diminished in DEQ\( \text{T} \) with respect to DMQ\( \text{T} \).

The cation radical in oligothiophenes longer than the trimer was found to exist mainly under the associated form of two cation radicals (\( \pi \)-dimers) [19] (see below). Thus, all the redox potentials will be corrected by the equilibrium constants of the \( \pi \)-dimerization process. However, in a comparative study of one series of oligomers the relative errors remain negligible [21].

Fig. 4. Variation of the oxidation potentials (\( E_1 \) and \( E_2 \)) with the reciprocal of the number of thiophene rings (\( N \)).
The voltammograms of the oligomers during successive oxidation/reduction cycles between 0 and 1.2 V present a flattening of the electrochemical response. This fact is associated with the presence of two parallel processes: a solubilization, and a chemical degradation of the oligothiophenes due to the presence of strong nucleophiles such as water, like contaminants in the electrolyte [20,29,30,34]. The solubilization can be seen as a subtle and yellow cloud around the electrode during every anodic sweep. The partial degradation promotes an increasing resistance of the film, observed as decreasing slopes on the consecutive voltammograms. The radical cations are stable under these experimental conditions during several cycles. Once oxidized by electrochemical polarization, the coated electrode extracted from the solution under anodic polarization, then rinsed and dried, solid oligomers are stable and keep their oxidized state for long periods of time. Thus, we have registered the FT-Raman spectra of these samples and found that they remain as radical salts for at least 1 month [35].

3.2. Spectroscopic study

The cation radical and dication electronic spectra of a number of unsubstituted and alkyl-substituted oligothiophenes in solution have been reported [36], but until now only very limited information has been available concerning the spectra in the solid state [23]. The radical cations show two bands, due to electronic excitations from HOMO to SOMO and from SOMO to LUMO, at wavelengths much longer than those of the neutral compounds. Usually these bands show a secondary peak or shoulder on the high-energy side assignable to vibronic transitions. According to selection rules, dications should present only one transition from HOMO to LUMO which appears usually with vibronic structure. The dication band is always located in between the two bands of the cation radical. In all the cases, as the oligomer length increases, the band shifts to longer wavelength due to the greater π-electron delocalization.

More recently, it has been shown that, when oligothiophene cation radicals are formed in polar solvents or at low temperature, diamagnetic charged species could also originate from the coupling of two radical cations, thus forming a so-called dimer-dication or π-dimer [21,22]. It has been shown that π-dimer formation is enhanced for longer oligomers, and that a substantial amount of dimeric species is already present at room temperature [22]. As expected, higher concentration also favored dimerization. The π-dimers show three bands in the Vis-NIR spectrum: (i) two π-π* bands shifted to shorter wavelength compared with the undimerized species, and (ii) a charge transfer transition, polarized along the axis joining the two cation radicals, at longer wavelength in the near-IR [37]. The π dimerization of cation radicals has also been discussed in the context of the formation of solid conducting radical salts [36-38].

The optical spectra of the various alkyl-substituted oligothiophenes were measured in a special spectroelectrochemical cell, described in Section 2. Figs. 5–7 show the visible spectra (between 500 and 1000 nm) of DMQqT, DMQqT and DMSxT films electrochemically oxidized at different potentials at room temperature. The application of an increasing positive potential and simultaneous recording of the optical absorption spectra show the evolution of visible absorption bands with increasing oxidation degree. Table 2 presents the values measured for the more important bands of the oligothiophenes studied in this work. Band positions for these transitions have been determined from difference spectra on the neutral material. As the morphology of the films changes during the oxidation experiment, we observe how the spectrum presents some irregularities (noise) due to this effect.

Fig. 5. Set of optical spectra (between 500 and 1000 nm) recorded during the oxidation of DMQqT.
Upon p-doping of DMQtT the radical cation dissolved slowly in this medium and an equilibrium between species in the solid state and in solution was established. The visible spectrum of the tetramer (Fig. 5) displays three bands at 533, 658 and 852 nm which are, in general, intensified as the potential increases; therefore, these bands are associated with monocationic species. Moreover, the central band decreases relatively to the others as the concentration of the cations increases, i.e., at higher potential values. Therefore, the side bands are attributable to a species arising from the association of the radical cations (π-dimers) which are responsible for the central band. The radical cation of chemically doped DMQtT, in solid state and solution, shows in this spectral range a single band about 680 nm [23]. On the other hand,
π-dimer bands have been assigned to methoxytetrathiophenes in acetonitrile solution at 550 and 855 nm [22]. Moreover, two absorption bands at 551 and 905 nm were assigned by Bauerle et al. [21] to π-dimers in a spectroelectrochemical experiment on an α,β-alkyl end-capped tetrathiophene solved in methylene chloride. Thus, under our experimental conditions, the radical cation of the DMQqT is partially associated with dimers. As expected from the electrochemical results, the spectral pattern of DEQtT is very similar, relative to that of the homologous DMQqT. The radical cation form of DEQtT shows a bathochromic shift of the respective absorption bands due to the higher electron-donating effect of the ethyl substituent.

The π-dimers are mainly generated in polar solvents where the aggregation of radical species is favored [22,36]. If we compare our visible spectrum of the thin film DMQqT radical cation in AN–TEAP solution (Fig. 6) with the spectrum of the DMQqT radical cation in a solution of dichloromethane–tetrabutylammonium perchlorate [25], we observe how the band measured at 550 nm in dichloromethane, assigned to π-dimers, is weaker than the band measured at 670 nm, assigned to monomer radical cation. In our results, the most intense band is assigned to π-dimers. The different behavior in the two solvents comes about because the more polar acetonitrile can disperse the charge and minimize the coulombic repulsions that result when two cation radicals come together in a π-dimer.

The typical absorption of the radical cation state in this spectral range is gradually shifted to lower energies when the oligomer π-system is extended; this trend becomes clearly apparent in going from DMQqT to DMQqT and DMSxT. In Fig. 6 we observe the spectra of DMQqT oxidized electrochemically at different potentials. The most intense band is measured at about 830 nm and we have assigned it to the monomer radical cation; around 773 nm a shoulder appears which we assign to a vibronic transition. In chemically doped DMQqT the radical cation band was assigned by Hotta et al. to 790 nm in the solid state and to 747 nm in CH₂Cl₂ solution. These different values are due to different synthesis conditions and solvent effects [15]. The band around 572 nm is the weakest of the spectrum, and we assign this band to a vibronic transition bands due to the higher electron-donating effect of the terminal α positions. Cyclic voltammetry on DMQqT reveals that the first oxidation potential is reversible and practically independent of the size of the terminal substituent. The cyclic voltammograms of DMQqT and DMSxT give two sets of anodic and cathodic peaks which reveal two reversible oxidation potentials. These two oxidation reactions are attributed to the successive formation of the radical cation and dication. Excellent inverse correlation is obtained between the redox potentials and the chain length. This reflects that the energy necessary to form the charged species decreases as the chain length increases. Moreover, all experimental points align along two lines that converge to roughly the same potential when 1/N = 0 (0.84 and 0.71 V for the first and second oxidation potentials, respectively). This indicates that, as the chain length increases, the energy needed to withdraw a second electron to an already oxidized oligomer decreases.

We have assigned the visible spectra of α,α'-dimethyl oligothiophenes registered 'in situ' with a spectroelectrochemical system where the redox process and the optical measurements are simultaneous. Inverse correlation is obtained between the transition energies and the chain length. This reflects increasing π-electronic delocalization with increasing number of thiophene rings for all species investigated. We have confirmed the presence of π-dimers in all of the oligomers; our investigations in the solid state on end-capped dimethyl oligothiophenes demonstrate the existence to radical cation species and its intensity increases with increasing potential.

During oxidation of DMSxT two new weak bands grow at 685 and 550 nm. Previous experimental observations on methoxyoligothiophenes indicate that the new absorbance at 685 nm is due to a cation radical dimer [22]. In every case the formation of π-dimers is accompanied by a blue shift of the absorption band of the monocation. We can conclude that the formation of π-dimers (533, 572, 685 nm) with increasing chain length of the oligomer is favored thermodynamically [21] and, on the other hand, is restricted by the lower solubility of the oxidized species. As has been pointed out by Hotta and Waragai [23], the spectroscopic features of the solid films differ from those for the solution in that the neutral HOMO–LUMO transition for the solid is given increasing intensity on the low-energy side at increasing oxidation level. In the solution spectra, however, the original π–π* absorption band of the neutral molecules is almost completely bleached at higher doping levels. According to these authors, one of the most likely explanations is that the spectroscopic features of the solid film result from molecular associates such π-dimers and π-stacks. Therefore, the band at 550 nm may be attributable to a species arising from the association of the radical cations.

4. Conclusions

We have carried out solid-state electrochemical measurements on oligothiophenes substituted by alkyl groups on the terminal α positions. Cyclic voltammetry on DMQqT reveals that the first oxidation potential is reversible and practically independent of the size of the terminal substituent. The cyclic voltammograms of DMQqT and DMSxT give two sets of anodic and cathodic peaks which reveal two reversible oxidation potentials. These two oxidation reactions are attributed to the successive formation of the radical cation and dication. Excellent inverse correlation is obtained between the redox potentials and the chain length. This reflects that the energy necessary to form the charged species decreases as the chain length increases. Moreover, all experimental points align along two lines that converge to roughly the same potential when 1/N = 0 (0.84 and 0.71 V for the first and second oxidation potentials, respectively). This indicates that, as the chain length increases, the energy needed to withdraw a second electron to an already oxidized oligomer decreases.

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of dynamic equilibria between monomers and dimers of radical cations. It can be assumed that the spatial proximity and favorable orientation of the molecules (radical cations) facilitate such intermolecular interactions in the solid state. The formation of dimer structures at such low concentrations of radical cations (monomers) has important implications for oxidized conducting polymers. In the solid polymer the cation radicals (polarons) are more concentrated, and there must be extensive intermolecular interactions of the type demonstrated here. Clearly, diamagnetic \( \pi \)-dimers or \( \pi \)-stacks can be an alternative to diamagnetic bipolarons in conducting polymers.

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