

Electrochemical Reactivity of Oligothiophenes and Estimation of Interchain Interactions

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Os oligotiofenos podem ser usados como modelos para a estocagem e o transporte de carga nos polímeros condutores eletrônicos. Nós apresentamos aqui o estudo eletroquímico de uma série de oligotiofenos curtos substituídos e deduzimos correlações entre as propriedades da molécula, o comprimento da cadeia e sua estrutura química. A voltametria cíclica foi empregada para formar reversivelmente os radicais cátions e os dicátions e os potenciais redox foram medidos em função de diferentes variáveis. Da dependência da temperatura e da concentração nós confirmamos a dimerização reversível dos radicais e estimamos a interação intercadeia do polímero.

Oligothiophenes can be used as models for the charge storage and transport in electronic conducting polymers. The electrochemical study of a series of short end-substituted oligothiophenes is reported and the correlations between the properties of the molecule, the chain length and its chemical structure are presented. Cyclic voltammetry was used to reversibly form the radical cations and dications, and the redox potentials were measured according to different variables. From the temperature and concentration dependences, the reversible dimerization of radicals was confirmed and the interchain interaction of the polymer was estimated.

Keywords: *oligothiophenes, cyclic voltammetry, redox potential, dimerization*

Introduction

Oligomers like oligothiophenes, have recently been studied to try to better understand the properties of electronic conducting polymers¹. The chemical assembly leads to molecules with well-defined structure and controlled conjugation length which show improved electronic properties in the solid-state². The electrochemical characterization of the oligothiophenes in solution can be used to correlate solid-state properties with the chemical structure of the compounds. The difficulties due to the high reactivity of the short oxidized oligomers and the low solubility of the larger species can be solved by the blocking of the

terminal positions and the lateral functionalization of the conjugated chains. Recent results based on spectro-electrochemical and RPE experiments³ showed that oligothiophenes radicals can reversibly dimerize even at low concentrations, leading the authors to suggest that π -stacks could be a reasonable alternative to bipolarons as conducting entities in oxidized conjugated polymers.

In order to investigate the reactivity of short oligomers, we synthesized a series of α,α' -oligothiophenes of the general formula $R-nT-R'$, where $R, R' = H, Br, NO_2, OMe$, and $n = 2, 3, 4$. The overall results of this electrochemical study are reported here; preliminary work and thin-film

properties of these compounds have been presented elsewhere⁴⁻⁶. High scan rate cyclic voltammetry was used to enhance the reversibility of the electrooxidation, and the variation of the redox potential in function of the chain length, the electronic nature of the substituent, the concentration and the temperature was investigated. The thermodynamic parameters of the dimerization of radical cations have been calculated and the implications for polymer properties are discussed.

Experimental

All reagents were commercially available and the various compounds were synthesized according to established procedures⁷. Bi- and terthiophenes were generally soluble in acetonitrile, while quaterthiophenes were dissolved in a 70/30 toluene/acetonitrile mixture; tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. The counter electrode was a Pt wire and the reference electrode was an aqueous saturated calomel electrode with a salt bridge. The working electrode was a gold (10 μm and 1 mm diameter) or a glassy carbon (3 mm diameter) disk. The temperature cell was controlled using a Dewar can and the reference electrode temperature was regulated to $20.0 \pm 0.1^\circ\text{C}$. Oxygen was removed from all solutions by bubbling argon. Instrumentation consisted of a PAR model 175 programmer, a home-built potentiostat⁸, and Nicolet 310, 415 oscilloscopes.

Results and Discussion

The reversible formation of radical cations and occasionally of dications was characterized by electrooxidation, adapting the scan rate to the species lifetime. With the increasing size of the π -system of the oligomers, the formal redox potentials are shifted to lower energies and the two processes come close together theoretically becoming energetically equivalent for an infinite chain (ideal polymer)⁹. On the other hand, the stabilization of the electrogenerated species by electron donor substituents was verified by lower redox potentials and longer lifetimes estimated from the scan rate, which was varied from 0.05 (Br-4T-OMe) to 8000 V/s (3T-Br). The substituent effect was rationalized by the empirical Brown equation for an aromatic series¹⁰, and the good agreements for the 3T and 4T series indicated that these electrochemical reactions are ruled by the same mechanism where electrical charge is stabilized by mesomeric effects (Fig. 1).

The monomer concentration ($[M] = [nT]$) dependence of the apparent redox potential (E_{ap}^0) of the first ionization of several oligomers was subsequently studied at low temperature in order to prove the existence of the dimer ($M_2 = (nT)_2$). See for example the case of Br-3T-Br in Fig. 2. A linear variation of E_{ap}^0 with regard to $\ln[M]$ was indeed observed, with a slope in agreement with a mechanism

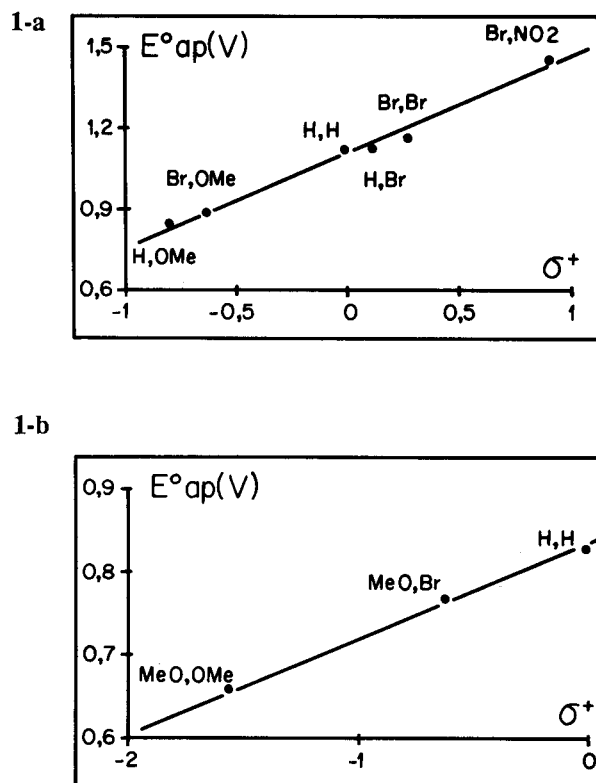
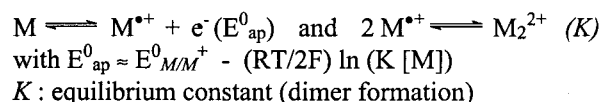


Figure 1. Variation* of the redox potential (first ionization) of oligothiophenes with the Brown coefficients ($T = 20^\circ\text{C}$): a) 3T series (CH₃CN); b) 4T series (70/30 Tol./CH₃CN). * $\Delta E_{\text{ap}}^0/E_{\text{ap}}^0 < 2.5\%$.

involving the fast reversible coupling of two radical-cations (π -dimer)¹¹:



The K value can be determined, for example, where the real redox potential becomes accessible, *i.e.* at low monomer concentration (Fig. 2) the deviation from the straight

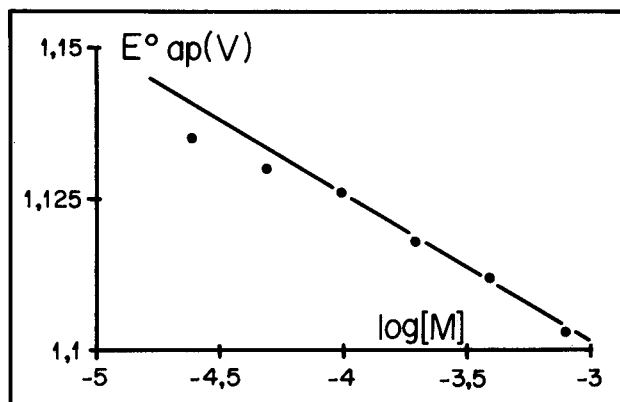


Figure 2. Variation of the apparent redox potential (first ionization) of Br-3T-Br with the concentration in 70/30 Tol./CH₃CN at -17°C .

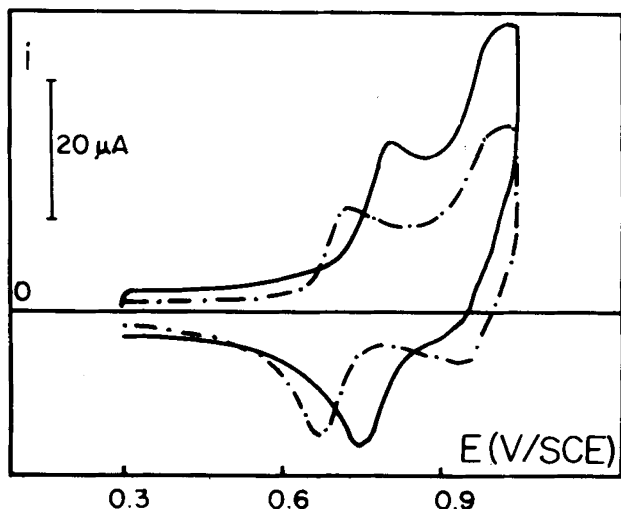


Figure 3. Cyclic voltammogram (0.2 V/s) of MeO-3T-Br ($[M] = 4.10^{-4}$ M) in 70/30 Tol./CH₃CN at -42 °C(---) and 12 °C(—).

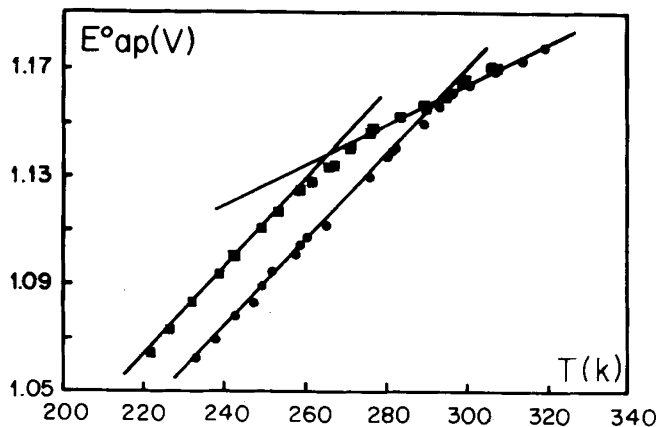


Figure 4. Variation of the apparent redox potential (first ionization) of Br-3T-Br with the temperature in 70/30 Tol./CH₃CN: $[M] = 9.10^{-5}$ M (■), $7.0.10^{-5}$ M (●).

Table 1. Thermodynamic parameters of the dimerization reaction of some selected oligothiophenes (**: CH₃CN solvent, *: 70/30Tol./CH₃CN solution).

Oligomer	K (M ⁻¹)	ΔG^0 (kJ.mol ⁻¹)	ΔS (J.K ⁻¹ .mol ⁻¹)
MeO-2T-OMe**	30	- 8	- 170 ± 40
Br-3T-OMe*	860	- 16	- 120 ± 20
Br-4T-OMe*	8600	- 22	- 100 ± 20

line is clearly observed. To complement the determination of the thermodynamic parameters, the variation of E^0_{ap} was studied for a large range of temperature. Typical voltammograms obtained at two different temperatures are shown in Fig. 3.

The substantial change in the position of the first process was in agreement with the proposed mechanism, where heating favors monomer existence. The redox potential can be related to entropic change by $\delta E/\delta T = \Delta S/F$, given that $\Delta G = -FE = \Delta H - T\Delta S$ (by convention, for a reduction monoelectronic process). Examining this variation two distinct entropic behaviors could be determined and interpreted as the monomer (Higher Temperature) and dimer (Lower Temperature) existence fields (Fig. 4). The ΔS associated with dimer formation from radicals can be deduced from the two slopes:

$$\Delta S (2M^{*+} \rightarrow M_2^{2+}) = 2F [(\delta E^0_{ap}/\delta T)_{HT} - (\delta E^0_{ap}/\delta T)_{LT}].$$

As expected, dimerization lowered entropy (ΔS). The thermodynamic parameters of some characteristic oligomers are presented in Table 1. The increase in entropy for the shorter oligomers could not be clearly evidenced due to some uncertainty in our determination method. However, the most interesting feature was the large variation of the K constant, from 30 for the 2T to 8,600 M⁻¹ for the 4T, which means that for low concentrations ($\sim 5.10^{-4}$ M) at ambient temperature the 2T remains in the monomer form while the 4T associates. This trend was also verified by the higher increase in the free enthalpy dimerization for the

larger molecules, possibly due to better delocalization of the charge in the long chains. A linear correlation was obtained between $\log K$ (or ΔG^0) and the inverse chain length which gave a stabilization energy (ΔG^0) of - 36 kJ.mol⁻¹ for the dimer form by extrapolation from the ideal polymer ($1/n = 0$). This high value means that strong interchain interactions should exist in the solid state oxidized polymer and could make a significant contribution to the electrical conductivity of these materials.

Conclusions

The electrooxidation of a series of end-substituted oligothiophenes by cyclic voltammetry was reported. We verified up to the tetramer that electron donor substituents lower the ionization potential of the molecules and stabilize the charge species in agreement with the Brown empirical equation; this suggested a unique reaction mechanism dominated by electronic mesomeric effect. The existence of a reversible dimerization between the radicals was confirmed by pure electrochemical data, and the thermodynamic parameters of the reaction were determined. By extrapolating from the infinite chain, the interchain interaction of charged polythiophene was estimated.

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