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Electrochemical Evidence of π-Dimerization with Short Thiophene Oligomers

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Several α,α′−disubstituted oligothiophenes of various lengths have been studied by cyclic voltammetry in a 30/70 acetonitrile/toluene mixture and in pure acetonitrile. The variation of the redox potentials with the temperature and the concentration allows the measurement of the thermodynamic parameters of the π-dimer formation reaction and therefore the π-dimer existence domain, even in the case of short oligomers. The extrapolation of the relation between the free energy of the π-dimer formation and the number of thiophene ring allows estimation of the interchain interaction between polarons in polythiophene.

Introduction

Thiophene oligomers in which thiophene units are linked by their α-positions have recently been the focus of much attention (see refs 1−20 and references therein). They hold promises in various fields dealing with molecular electronics (see, for example, refs 4 and 11 and references therein), but they are also good models for studying charge storage in conducting polymers. In several cases, the radical cations of oligothiophenes have been produced by chemical oxidation in solution and characterized in carefully controlled conditions.[3,6] Such investigations suffer from the reactivity of oligothiophene radical cations in solution when the number of thiophene units is small and from the low solubility of higher oligomers. For example, if the radical cation of the unsubstituted quaterthiophene is observed through the reversibility of its oxidation wave in fast-scan cyclic voltammetry experiments, the unsubstituted terthiophene exhibits only irreversible voltammograms in the same conditions.[13] This problem may be overcome by blocking the reactive α-positions and the formation of many stable radical cations by electrochemical oxidation of such compounds has been reported.[5−19] Substituent effects on the stability of these radical cations was studied and it was found that the lifetimes are longer when the substituents are donor groups[19] and with the higher oligomers.[6,16,17,19] In some cases, with some disubstituted oligomers, even the dications were stable during the time of a slow-scan cyclic voltammetry (v = 0.1 V s^{-1}).[6−11,13,14,16,17,19]

Recently, on the basis of spectroelectrochemical and ESR experiments with substituted terthiophenes, Miller and co-workers have proposed that the radical-cations of oligothiophenes exist in the form of either a monomer of a π-dimer depending on concentration and temperature conditions.[8−10] This point is of great importance because π-dimers and π-stacks could be responsible for

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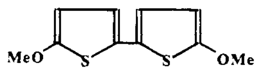
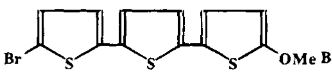
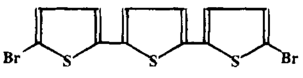
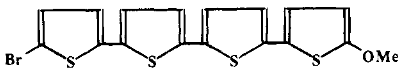
the properties of oxidized polythiophene and other conducting polymers.[10] These intermolecular π-interactions may be strong in thin films and provide a mechanism for electrical conductivity. Similar experiments performed by other authors have confirmed Miller's results with other oligothiophenes.[15,16,18] In a preliminary work, we have recently shown that the existence of the π-dimer can be demonstrated with the determination of all the thermodynamic parameters for the oxidation of the α-bromo-α′-methoxyquaterthienyl only by analyzing the temperature and concentration dependence of the redox potentials.[13] However, the time scale for the observation of electrogenerated species is usually shorter for cyclic voltammetry than for spectroelectrochemical studies. As a consequence, the former method allows the study of more unstable oligothiophene radical cations:[21]


MeO-2T-MeO


Br-3T-MeO


Br-3T-Br


Br-4T-MeO

After having examined the dimerization of a quaterthienyl, it is suitable to investigate the behavior of smaller oligothiophenes, namely, some ter- and bithienyls. It is interesting to know not only if the existence of π-dimers is a general property of all thiophenic radical cations but also how it depends on the length of the conjugated chain and on the nature of the α-substituent. In the case of short oligomers, cyclic voltammetry becomes the only suitable investigation mean because of the short lifetimes of the generated species. We have examined the electrochemical behavior of the oligothiophenes below, determined the thermodynamic parameters for their oxidation, and compared them with the results previously obtained for Br-4T-MeO.[13] The implications and possible developments of these results are discussed in the following parts.

Experimental Section

Chemicals. The different oligothiophenes have been synthesized according to previously published procedures.[22] The solvent (70/30 toluene/acetonitrile mixture) was used to increase the solubility of the aromatic compounds, with 0.1 M tetrabutylammonium perchlorate (Fluka Puriss) added as supporting electrolyte. When the oligothiophene was soluble enough, for comparison purpose, pure acetonitrile (with the same electrolyte) was also used. Its larger conductivity allows the use of higher scan rates in cyclic voltammetry experiments.

Cell and Electrodes. The counter electrode was a Pt wire and the reference electrode an aqueous saturated calomel electrode ($E°$/SCE = $E°$/NHE − 0.2412 V) with a salt bridge containing the supporting electrode. The working electrode was a 3-mm-diameter disk glassy carbon obtained by sealing in a glass holder a 3-mm carbon rod (Tokaï Corp.). The SCE electrode was checked against the ferrocene/ferricinium couple ($E°$ = +0.405 V/SCE) before and after each experiment. All the potentials are reported versus SCE.

Instrumentation and Procedures. For temperature dependence experiments, the cell was tightly sealed and simply dipped into a Dewar can filled with acetone (for low $T°$) or water (high $T°$), the temperature of which was controlled by the addition of dry ice or hot water. Before each measurement, the system was equilibrated for 5−10 min and the temperature inside the cell was monitored by a digital thermometer. The reference electrode was as previously described[13] thermostated at 20 °C by an independent circulation of water. As discussed in ref 23, such arrangement leads to a negligible contribution (less than 0.03 mV/K) of the thermal junction potential to the variation of the measured redox potential with the temperature.

Electrochemical instrumentation consisted of a PAR Model 175 Universal programmer and of a home-built potentiostat equipped with a positive feedback compensation device.[24] The cathodic and anodic peaks were measured on 310 Nicolet digital oscilloscope. From repetitive measurements, the error made on the relative determinations of $E°_{app}$ during one set of temperature variation was estimated to be better than ±3 mV. Accuracy on slopes for the temperature variations are the calculated standard deviations taking into account this error on each potential measurement.

The integral equation for a reversible DIM1 mechanism was carried out numerically, dividing the interval $0-\tau$ into 4000 subintervals using the same linearizations than in ref 25. Calculations were made on PC 486DX50 microcomputer.

Results and Discussion

In a preliminary communication,[13] we reported that MeO-4T-Br gives stable radical cations in a toluene/acetonitrile mixture even at the lowest scan rates (v = 0.1 V s^{-1}), and that at room temperature, the radical cation exists under the form of a π-dimer. In this study, we examined the electrochemical behavior of two α,α′-disubstituted terthiophene (MeO-3T-Br and Br-3T-Br) and of a α,α′-disubstituted bithiophene MeO-2T-MeO. In acetonitrile/toluene mixture and at room temperature, MeO-3T-Br exhibits a reversible first oxidation voltammogram at scan rate of 0.1−0.2 V s^{-1} followed by the irreversible formation of the dication (see Figure 1). For Br-3T-Br and MeO-2T-MeO, a reversible voltammogram could also be obtained, but at a slightly higher scan rate (0.5−1.0 V s^{-1}) showing a lesser stability of the generated radical cation.

Electrochemical Studies of Disubstituted Terthiophenes. We have chosen to perform detailed electrochemical studies of the first oxidation system of MeO-3T-Br and Br-3T-Br in acetonitrile/toluene mixture and in pure acetonitrile. These two compounds are sufficiently soluble (>10^{-3} M) in the acetonitrile/toluene mixture to investigate a significant variation of the concentration scale while still retaining a sufficiently large electrochemical signal. Unfortunately, only MeO-3T-Br is soluble in pure acetonitrile at low temperature.

In the acetonitrile/toluene mixture, the variations of the apparent $E°_{app}$ (measured as the midpoint between the anodic and cathodic peaks) with the initial oligomer

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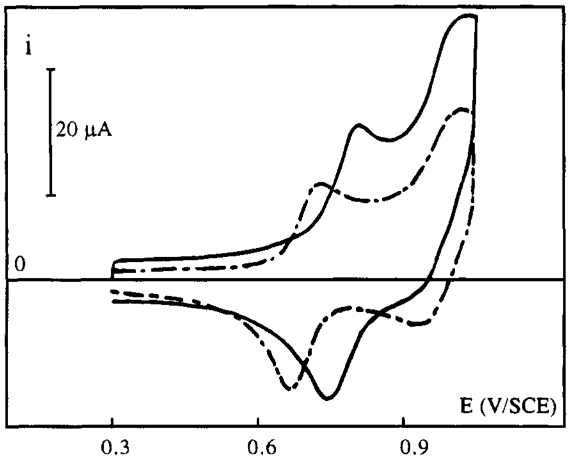

Figure 1. Cyclic voltammetry on a glassy carbon electrode (diameter 3 mm) of a solution of MeO-3T-Br ($C° = 6 \times 10^{-4}$ mol L^{-1}) in a 70/30 toluene + acetonitrile mixture (+0.1 M NBu_4ClO_4) at 25 (—) and at −45 °C (– • –). Scan rate $v = 0.2$ V s^{-1}. E in volts vs SCE.

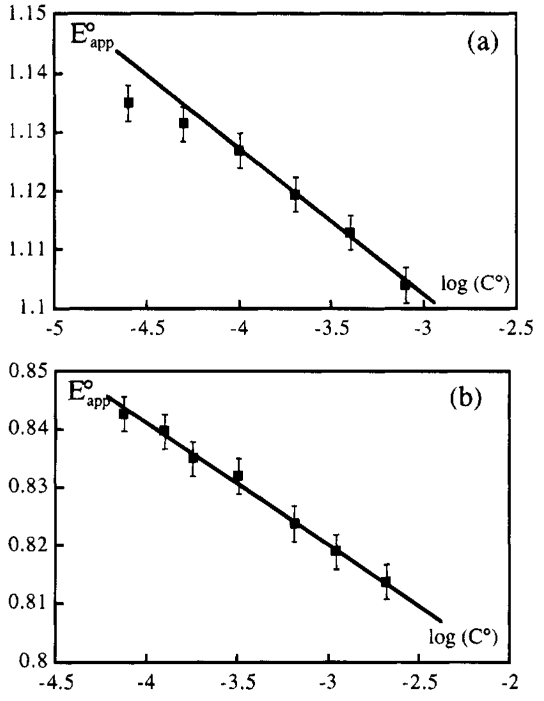

Figure 2. Cyclic voltammetry on a glassy carbon electrode (diameter 3 mm) in a 70/30 toluene + acetonitrile mixture (+0.1 M NBu_4ClO_4) at −17 °C. Scan rate $v = 0.2$ V s^{-1}. Variation of $E°_{app}$ (in volts vs SCE) with the initial concentration of oligomer (in mol L^{-1}). (a) Br-3T-Br, (b) MeO-3T-Br.

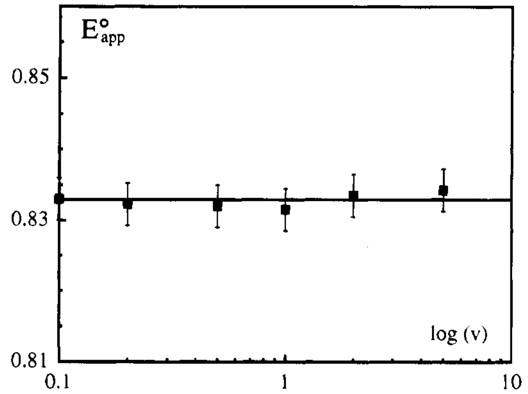

Figure 3. Cyclic voltammetry on a glassy carbon electrode (diameter 3 mm) of a solution of MeO-3T-Br ($C° = 3.2 \times 10^{-4}$ mol L^{-1}) in acetonitrile (+0.1 M NBu_4ClO_4) at −17 °C. Variation of the $E°_{app}$ (in volts vs SCE) with the scan rate (in V s^{-1}).

concentration (between 5×10^{-5} and 10^{-3} M) were performed at a low temperature ($T = -17$ °C) to favors the possible existence of a dimer. In such experiments, it is better to examine the variations of $E°_{app}$ than the variations of the anodic peak potential. They are less sensitive to the influence of the residual ohmic drop and to the heterogeneous electron-transfer kinetics due to a mutual compensation of their effects on the anodic and cathodic peak.[26]

As shown in Figure 2, a linear variation is obtained for the variation of $E°_{app}$ for the two oligomers in function of log($C°$). The data for Figure 2 and for all the others measurements were for scans limited to the first peak only. For the higher concentrations, slopes of −25 and −21 mV/decade of $C°$ were found for Br-3T-Br and Br-3T-MeO. We have also checked that at this temperature $E°_{app}$ remains constant with the scan rate. This is clearly demonstrated with MeO-3T-Br for which the radical cation is quite stable. To ascertain this point, we chose to work in pure acetonitrile because the conductivity of this solvent is still high even at this low temperature, and therefore the relative absence of ohmic drop allows us to determine unambiguously the redox potential value. The variation of $E°_{app}$ (Figure 3) shows almost no variations between 0.1 to 10 V s^{-1} at a concentration of 3.2×10^{-4} mol L^{-1}; it indicates that no effects due to the dimerization or heterogeneous charge-transfer kinetics are observed on the measured $E°_{app}$ values and also that our measurements are not disturbed by the residual uncompensated ohmic drop. As expected for a diffusion controlled process, in this range of scan rate, the peak current exhibits a linear variation with the square root of the scan rate.[21] All these results are in agreement with the theoretical behavior for a mechanism involving the fast reversible coupling of two radical cations to form a dimer ($DIM1_{rev}$):[26–28]

$$\text{Br-3T-X} - e^- \rightleftharpoons \text{Br-3T-X}^{\bullet +}$$

$$2\text{Br-3T-X}^{\bullet +} \rightleftharpoons \pi\text{-dimer}$$

This kinetics situation, corresponding to a diffusion controlled behavior with a totally mobile equilibrium (the voltammogram is completely reversible) is quite common in organic electrochemistry and several examples have already been reported (see, for example the oxidation of substituted phenolates[29,30]). A semianalytical expression for the voltammogram $i = fn(E)$ can be obtained which is (written with the adimentional parameters:[28]

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$$\pi^{-1/2}\int_0^{\tau}\psi(\eta)(\tau-\eta)^{-1/2}\,\mathrm{d}\eta = \{[4+\exp(-2\xi^*)]^{1/2} - \exp(-\xi^*)\}^2/4$$

with (for an oxidation process) $\tau = (E - E_i)F/RT$, $\psi = i/[FSC^\circ(DF_v/RT)^{1/2}]$, $\xi^* = (F/RT)(E - E^\circ{}_{3T^{\bullet+}/3T}) + {}^1/_2 \ln(2KC^\circ)$, S the electrode area, v the scan rate, C° the initial concentration of monomer, R the gas constant, F the Faraday number, and T the absolute temperature, $E^\circ{}_{3T^{\bullet+}/3T}$ is the normal potential of the considered terthiophene radical cation/terthiophene couple, E and E_i the applied and initial potentials to the working electrode. This equation can be solved with a numerical method (see Experimental Section). If the direction of the scan is reversed at a potential at least 200 mV more positive than the peak potential, we obtain the following values for the adimentional peak potentials $\xi^*_{\mathrm{pf}} = 1.04$, $\xi^*_{\mathrm{pb}} = -0.59$, $\xi^*_{1/2} = (\xi^*_{\mathrm{pf}} + \xi^*_{\mathrm{pb}})/2 = 0.225$ (respectively for the forward scan, backward scan and midpoint peak potentials). In this analysis, we have neglected the term involving the difference of all diffusion coefficients on the $E_{1/2}$ value. This term is quite small and has been estimated to be around 2 mV,[28,29] which is smaller than the experimental error. In such conditions, the variation of $E^\circ{}_{\mathrm{app}}$ with C° and the equilibrium constant for the formation of the dimer K is immediately derived as (see ref 21 for the $KC^\circ \ll 1$ subcase):

$$-KC^\circ \gg 1\ E^\circ{}_{\mathrm{app}} = E^\circ{}_{3T^{\bullet+}/3T} - \frac{RT}{2F}\ln(KC^\circ) - 0.12\frac{RT}{F},$$

$$\Delta E_{\mathrm{p}} = E_{\mathrm{pf}} - E_{\mathrm{pb}} = 1.63\frac{RT}{F}$$

$$-KC^\circ \ll 1\ E^\circ{}_{\mathrm{app}} = E^\circ{}_{3T^{\bullet+}/3T},$$

$$\Delta E_{\mathrm{p}} = E_{\mathrm{pf}} - E_{\mathrm{pb}} = 2.22\frac{RT}{F}$$

Consequently when $KC^\circ \gg 1$, a slope of $-2.3RT/2F$ for the variation of $E^\circ{}_{\mathrm{app}}$ by decade of C° is expected which corresponds to a slope of −25 mV at −17 °C close to what we found for the two terthiophenes.

At low concentrations, a deviation from the straight line is clearly observed in Figure 2a, indicating that the dimer is no longer the major species in such conditions ($KC^\circ < 1$). From this change of behavior, we could estimate the equilibrium constant to be in the range of 2×10^4 L mol^{-1} at −17 °C and from the results of Figure 3 that the π-dimerization rate constant must be larger than 10^8 L mol^{-1} s^{-1} (using the kinetic zone diagrams in p 8 of ref 28). These values are compatible for the formation of such π-dimer which should involve relatively weak bond formation.

To obtain a measurement of the equilibrium constant for the dimer formation at room temperature, we need to measure the normal potential for $E^\circ{}_{3T^{\bullet+}/3T}$ and to establish the experimental conditions where the monomer is the major species existing in solution. As we did previously for MeO-4T-Br, a convenient way to determine these domains is to study the variation of the $E^\circ{}_{\mathrm{app}}$ in a large range of temperature. Figure 4 presents the variations of $E^\circ{}_{\mathrm{app}}$ for the two terthiophenes for T° varying between −40 and 35 °C and for different initial concentrations of monomer. According to the temperature domain, two straight lines with different slopes are observed.

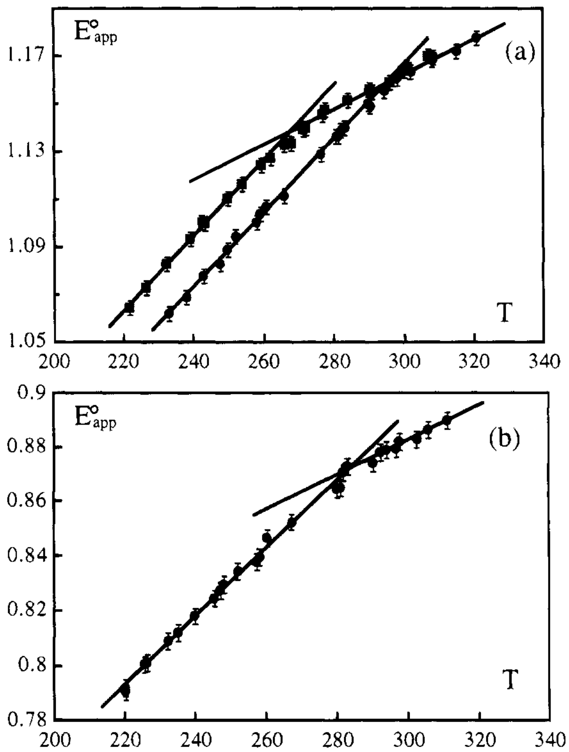

Figure 4. Cyclic voltammetry on a glassy carbon electrode (diameter 3 mm) in 70/30 toluene/acetonitrile mixture (+0.1 M NBu_4ClO_4) at −17 °C. Variation of the $E^\circ{}_{\mathrm{app}}$ (in volts vs SCE) with the absolute temperature. (a) Br-3T-Br $C^\circ = 9 \times 10^{-5}$ mol L^{-1} (■), 7×10^{-4} mol. L^{-1} (●), (b) MeO-3T-Br $C^\circ = 5.7 \times 10^{-4}$ mol L^{-1} (●).

The potentials of electrochemical reactions vary with the temperature (for an example of such a study see ref 31), with the variation being proportional to the entropy of the reaction according to Vant'Hoff's law written for a reduction process (electrochemical convention):[31,32]

$$\Delta G = -FE = \Delta H - T\Delta S$$

That is

$$\partial E_{\mathrm{app}}/\partial T = \Delta S/F$$

However, the variation (entropy) is different for the electrochemical couple: $3T^{\bullet+} + e^- \rightleftharpoons 3T$ and for the couple: $^1/_2$ dimer + $e^- \rightleftharpoons 3T$. Consequently, the two domains of temperature observed in Figure 4 can be interpreted as the field of existence of the monomer (high temperature) and of the π-dimer (low temperature). From these results, we can conclude that at room temperature the two terthiophenes exist in the form of a single radical-cation monomer for concentrations up to 10^{-3} mol L^{-1}. This result justifies in addition that the redox potentials that were measured by cyclic voltammetry in such conditions, correspond effectively to the couple $3T/3T^{\bullet+}$.[19]

The slopes $\partial E_{\mathrm{app}}/\partial T$ for the different temperature domains are recorded in Table 1. As expected, the slope at low temperature is higher because the entropy of formation of the dimer is greater than that for the formation of the single radical cation. From these

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Table 1. Thermodynamic Parameters for the Different Thiophene Oligomers

oligomer	solvent	$C°$ (mol L^{-1})	$\partial E_{app}/\partial T^a$ (high $T°$)	$\partial E_{app}/\partial T^a$ (low $T°$)
MeO-2T-MeO	ACN	5.4×10^{-4}	0.55 (±0.03)[b]	1.44 (±0.2)[b]
Br-3T-MeO	ACN	6.2×10^{-4}	0.63 (±0.06)[b]	1.56 (±0.03)[b]
Br-3T-MeO	ACN/ toluene	5.7×10^{-4}	0.64 (±0.06)[b]	1.25 (±0.05)[b]
Br-3T-Br	ACN/ toluene	7.0×10^{-4}	0.69 (±0.2)[b]	1.54 (±0.03)[b]
Br-4T-MeO	ACN/ toluene	4.0×10^{-4}	0.64 (±0.05)[b]	1.41 (±0.07)[b]

[a] In mV K^{-1}. [b] Standard deviation.

values, the entropy values for the reaction of formation of the dimer from two radical cations: ($2 \times 3T^{\bullet +} \rightarrow$ dimer) can be extracted from

$$\Delta S = 2F[(\partial E°_{app}/\partial T)_{highest\ T°} - (\partial E°_{app}/\partial T)_{lowest\ T°}]$$

with the slopes reported in Table 1. This procedure eliminates the entropic contribution of the electron transfer for the oligothiophene/oligothiophene cation radical couples and also all temperature linear effects (arising for example from junction potential) that could disturb the individual entropic measurements at high and low temperatures. The equilibrium constants at room temperature are calculated from

$$K = \exp\left[\frac{2F}{RT}(E^{\circ 293K}_{nT^{\bullet+}/nT} - E^{\circ 293K}_{app}) - 0.24\right]$$

where $E^{\circ 293K}_{app}$ and $E^{\circ 293K}_{nT^{\bullet+}/nT}$ are the values of the redox potentials calculated from the extrapolation at 20 °C of the low- and the high-temperature variations. This procedure leads to a quite good accuracy for the determination of the equilibrium constant for most oligothiophenes, because the intercepts of the straight plots are usually close to the room temperature. However, in the case of MeO-2T-OMe, the intercept occurs at a low temperature and the extrapolation makes the $\Delta G°$ value obtained more of an estimation. The enthalpy values ΔH for the dimer formation are estimated from $\Delta H = RT \ln K + T\Delta S$. The thermodynamic parameters for the oligoterthiophenes are recorded in Table 2. The ΔS measured for the two terthiophenes (Br-3T-MeO and Br-3T-Br) are in the same range of what was previously reported for some other oligoterthiophenes in CH_2Cl_2 like Me-3T-Me (ΔS = 105 J K^{-1} mol^{-1}, ΔH = 42 kJ mol^{-1})[10] or for some end-capped oligothiophenes (ΔH in the range 42–65 kJ mol^{-1} according to the oligomer[16]).

If there were no interference of the residual ohmic drop or of the electron-transfer kinetics, the difference between the forward and the backward scan peak potentials $\Delta E_p = E_{pf} - E_{pb}$ would be expected to be smaller for a reversible dimerization mechanism than for a simple one-electron transfer. We have investigated this difference for the oxidation of MeO-3T-Br in acetonitrile which is a conducting solvent and therefore minimizes the residual ohmic drop (see Table 3). For temperatures in the range 280–250 K, ΔE_p values are very close to the theoretical difference expected for $^1/_2$ dimer + $e^- \rightleftharpoons$ 3T. At the highest temperature, ΔE_p increases, approaching the peak separations expected for a single electron-transfer voltammogram. This indicates that for this temperature, the dimer is no longer the major species in solution in agreement with the temperature domains displayed on Figure 4. The increase observed at the lowest temperature is maybe due to the influence of the electron transfer kinetics or rather to difficulties to compensate exactly the ohmic drop when the resistance of the working electrode becomes too large at low temperatures. With most of the other oligomers at room temperature, values around 50 mV are usually measured, which is in agreement with a similar mechanism, with the observation distorted by the influence of uncompensated residual ohmic drop in the toluene/acetonitrile mixture.

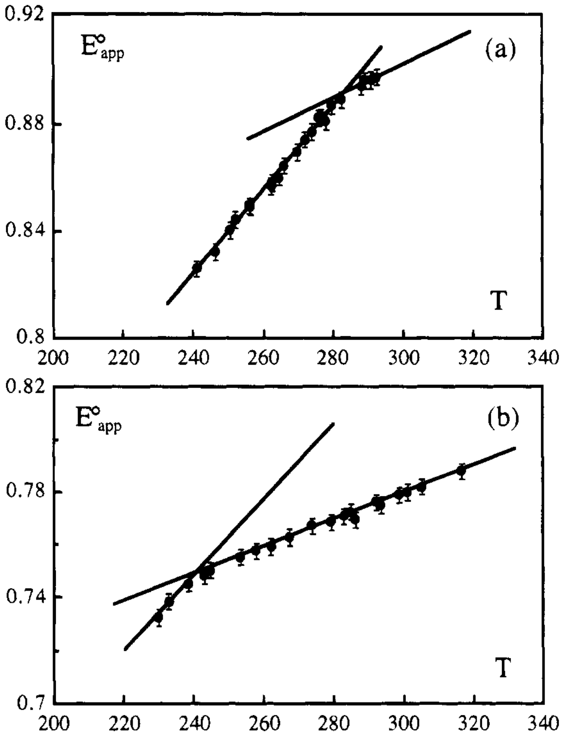

Figure 5. Cyclic voltammetry on a glassy carbon electrode (diameter 3 mm) in acetonitrile (+0.1 M NBu_4ClO_4) at −17 °C. Variation of the $E°_{app}$ (in volts vs SCE) with the absolute temperature. (a) MeO-3T-Br $C°$ = 6×10^{-4} mol L^{-1}, (b) MeO-2T-MeO $C°$ = 5.4×10^{-4} mol L^{-1}.

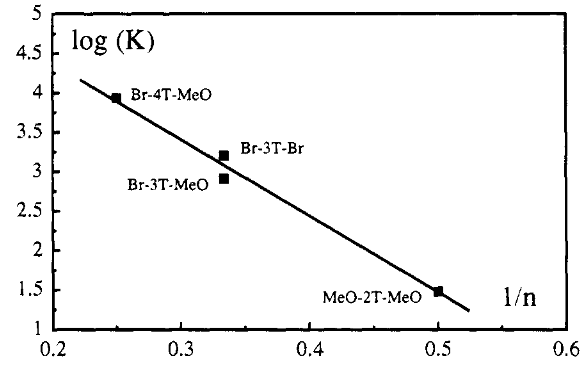

Figure 6. Variation of the π-dimerization equilibrium constant, K, at 293 K as a function of $1/n$ for the different oligothiophenes (n: number of thiophene units).

For seek of comparison with other oligothiophenes, the temperature variations experiments were performed with Br-3T-MeO in pure acetonitrile because this compound is fairly soluble in this solvent. The variations of $E°_{app}$ with the temperature are represented in Figure 5a. Similarly to what is observed in the ACN/toluene mixture, two straight lines are visible showing that the π-dimer also exists in pure acetonitrile. The slopes at

Table 2. Thermodynamic Parameters for the Different Thiophene Oligomers

oligomer	solvent	K_{293} (mol L^{-1})	$\Delta G°_{293}$ (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
MeO-2T-MeO	ACN	30	−8	−60	−170 (±45)
Br-3T-MeO	ACN	670[a]	−16[b]	−69 (±8)	−180 (±17)
Br-3T-MeO	ACN/toluene	860[a]	−16.5[b]	−51 (±9)	−118 (±21)
Br-3T-Br	ACN/toluene	1600[a]	−18[b]	−66 (±15)	−164 (±45)
Br-4T-MeO	ACN/toluene	8700[a]	−22[b]	−65 (±10)	−148 (±23)

[a] Error: ±50%. [b] Error: ±1.2 kJ mol^{-1}.

Table 3. Variation of $\Delta E_p = E_{pf} - E_{pb}$ with the Absolute Temperature (Oxidation of MeO-3T-Br in ACN)

T (K)	$(E_{pf} - E_{pb})^a$	$(E_{pf} - E_{pb})^b$	$(E_{pf} - E_{pb})^c$
295	50	56.5	41.5
281	39.5	53.8	39.4
273	38.5	52.1	38.2
260	33	49.7	36.4
250	34	47.8	35
237	39	45.3	33.3

[a] $C° = 1.2$ mol L^{-1}. Error ±3 mV. [b] Theoretical value for a one-electron reversible transfer. [c] Theoretical value for a reversible dimerization mechanism.

high temperatures which correspond to the existence domain of the monomeric species are similar in pure ACN and in the ACN/toluene mixture. The slope corresponding to the existence domain of the dimer in ACN is slightly steeper than in the ACN/toluene mixture as the result of higher values for the dimer formation enthalpy and entropy values. However, the equilibrium constant K at room temperature remains almost the same in the two solvents.

Electrochemistry of Disubstituted Oligodithiophenes. The reactivity of radical cations is higher for dithiophenes than the observed reactivity for ter- or quaterthiophene.[6,16,19,20] However, the α,α′-dimethoxydithiophene exhibits a reversible first oxidation for scan rates higher than 1 V s^{-1} at room temperature. We have studied the variation of its redox potential in function of the temperature in pure acetonitrile. As appears on Figure 5b, in the main part of the temperature domain, a linear variation is observed with a slope close to the values found at high temperatures for quater- and terthiophene oligomers. Only at the lowest temperature, a few points deviate from the main slope. These results indicate that oxidized dithiophene exists mainly under the form of a monomer across most of the temperature range in acetonitrile and consequently that the dimer has a low formation constant. Even if it is difficult to obtain a good accuracy for the slope corresponding to existence of the dimer, the point at the lowest temperatures allows us to estimate the value of K by the same procedure used for quater- and terthiophenes. A value around 30 M^{-1} is found which is much below the values found for the other oligomers.

Discussion

From Table 2, it is clear that the value of the equilibrium constants for the formation of the dimer at room temperature increases with the number of thiophene units in the oligomer. We could observe that at room temperature bi- and terthiophenes exist under the monomer form and on the contrary quaterthiophene under the dimer form. It is likely that for higher oligomers the major species in solution is also the π-dimer. The K values vary in a large range from 30 M^{-1} for the MeO-2T-MeO to 8700 M^{-1} for the Br-4T-MeO which corresponds to a change around 14 kJ mol^{-1} for the free energy at 293 K. One of reasons for this effect could be related to a better delocalization of the charge in long chain and that the coulombic repulsion decrease as it was observed from spectroscopic measurements.[16] Quantitatively, if we plot the variations of log(K) (or of the free energies) in function of $1/n$ (n: number of thiophene units) a linear correlation is found between these two values as usually found for electronic or electrochemical parameters in thiophene oligomers series[33] (see also for examples of such correlations ref 6 and 15−18). From this empirical linear relation, we can extrapolate to $1/n = 0$ to estimate a stabilization energy ($\Delta G°$) of such a dimeric form in an ideal polymer with a hypothetical infinite chain length which would lead to a stabilization energy of −36 kJ mol^{-1}. In such extrapolation, the role of solvent on the stability of the π-dimer is not taken into account. If we consider the high stabilization energy of the associated form, these interactions are probably comparable in solvent wet polythiophene; even in the dry polymer, interactions should also exist, although it is difficult to estimate to which extent. As it was proposed by Miller,[10] they may explain some of the properties of polythiophene, especially, the fact that only small ESR signals are observed with highly oxidized polythiophene.[34] They were also proposed by analogy with charge-transfer salts as the conducting entities in polythiophene.[10,16]

About the individual enthalpic and entropic contributions, our measurements of ΔH lead to an approximate constancy of ΔH values and ΔS values. Although our way of measurement in this particular case is affected by some uncertainty (linked to the determination method), we did not see any trend when proceeding from MeO-2T-MeO to Br-4T-MeO in apparent disagreement with the UV spectroscopic measurements of Baüerle for end-capped oligothiophenes.[16] About entropic contributions for the formation of the single radical cation, the values of the slopes for the variation of $E°_{app}$ with $T°$ obtained at high temperatures (corresponding to the monomer) are in the same range for all the oligomers. We think that this is justified by the fact that the entropy should remain the same for all the electron transfers between the oligomer and the monomeric radical cation for species which are very similar. Due to the uncertainties on the ΔH and ΔS determinations, it is therefore not possible to conclude whether the trend observed in the evolution of the ΔG values with the oligomer length is attributable to an enthalpic or to an entropic contribution.

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Conclusion

We have shown that cyclic voltammetry provides a useful tool for the study of the π-dimer formation in cases of short thiophenes oligomers, where the poor stability of the electrogenerated cation radicals forbids the use of spectroscopic methods. In addition, it has been possible to determine all the thermodynamic parameters of the dimerization reaction, only by the analysis of the electrochemical data with temperature variations, with a fair precision in the case of the equilibrium constants and the entropies. The extrapolation of the variation of the free energies with the number of rings allows to estimate the value of the interchain interaction in polythiophene when neglecting the role of solvent.

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