Thiophene Oligomers as Polythiophene Models. 2. Electrochemistry and in Situ ESR of End-Capped Oligothienyls in the Solid State. Evidence for π-Dimerization of Hexameric Polarons in Polythiophene

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Thin films of thiophene oligomers (n = 4, 6, 8, and 10) methyl-protected toward anodic coupling at the terminal α positions were investigated by cyclic voltammetry and in situ ESR in acetonitrile. Reversible oxidation goes from a single one-electron step (tetramer) to a single two-electron step (octamer and decamer) through two separate one-electron steps (hexamer). ESR indicates strong magnetic dimerization for the one-electron-oxidized hexamer. The close resemblance of the electrochemical and ESR behavior of the hexamer with that of polythiophene suggests that oxidation of the latter occurs via hexameric spin-dimerized polarons. The hexameric model is discussed taking account of the oligomeric nature of polythiophene.

Introduction

Actual research on the basic features of polyconjugated conducting polymers is for a large extent devoted to the study of selected oligomers in order to understand, with the help of molecular models, several unravelled questions put from this intriguing class of materials. Thiophene oligomers, due to their possible application as materials for nonlinear optics with particular environmental stability,[1] have been extensively investigated by IR spectroscopy,[2–4] solution electrochemistry,[5–8] solution ESR[9–11] UPS,[12] and UV–vis spectroscopy.[13,14] From an electrochemical point of view, polythiophene PT itself displays a yet unraveled odd behavior as its cyclic voltammogram shows a single oxidative step while the reduction of the oxidized form occurs in two isoelectronic processes.[15] This feature, which was observed also in the forward oxidative step of some alkyl-substituted polythiophenes[16] was first attributed to a still undefined rearrangement[15] and then specifically to the consecutive formation of polaron and bipolaron states accompanied by conformational relaxations.[17] At difference, on the basis of ESR results, we have found that PT is oxidized in two isoelectronic steps to two bipolaron states through a polaron state at the first step,[18] though we have not been able to give an explanation to the phenomenon. The puzzle is more evident if we consider that the analogous heterocyclic polymer polypyrrole is oxidized to a bipolaron state through a polaron state in a single redox process.[19,20]

In the course of a recent electrochemical investigation on the kinetics of anodic coupling of one-side methyl-protected thiophene oligomers,[21] we were able to obtain thin films of end-capped tetramer (Me_2T_4), hexamer (Me_2T_6), octamer (Me_2T_8), and decamer (Me_2T_{10}) on electrodes. This enabled us to perform an electrochemical and ESR investigation on PT model compounds in the solid state, i.e. in a physical form more closely related to the polymer than the solution state, and without complications due to further coupling processes, with the aim of a better understanding the problematic electrochemical behavior of polythiophene.

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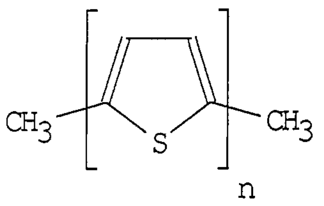

Me_2T_n $n = 4,6,8,10$

Experimental Section

Chemicals and Reagents. The preparations of 5-methyl-2,2′:5′,2″-terthiophene (MeT_3), 5-methyl-2,2′:5′,2″:5″,2‴-quaterthiophene (MeT_4), 5-methyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (MeT_5), and 5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (Me_2T_4) were reported previously.[21] α-Sexithenyl was prepared as in the literature.[22]

Thin films of Me_2T_4 were deposited by dip coating from a 10^{-3} M solution in CH_2Cl_2, α-sexithenyl films by sublimation under vacuum. Films of α-dimethyl-substituted thiophene hexamer, octamer, and decamer (Me_2T_6, Me_2T_8, and Me_2T_{10}) were electrodeposited on the electrode by oxidative dimerization of MeT_3, MeT_4, and MeT_5 respectively as reported previously.[21] Typically the electrode is immersed in a 1×10^{-3} M solution of the monomer in 0.1 M TBAP 1,2-dichloroethane (DCE) at 25 °C (1×10^{-4} M and 70 °C for MeT_5 due to the low solubility and slow coupling rate) and the potential cycled at 100 mV/s between 0.0 and 0.8 V vs Ag/Ag^+. After the passage of the desired amount of charge (in the range 5–100 mC/cm²) the electrode is washed with DCE and dried. IR and mass spectrometry confirmed the formulation of the compounds[21] while SEM analysis showed that the films are constituted by aggregates of blade-shaped microcrystals similar to those of Me_2T_4.[23]

Acetonitrile (AN) was distilled twice over CaH_2. The supporting electrolyte tetraethylammonium perchlorate (TEAP) was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received.

Apparatus and Procedure. Experiments were performed in 0.1 M TEAP AN under nitrogen and at 25 °C in three electrode cells. The counter electrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in AN (0.34 V vs SCE).

The working electrode for cyclic voltammetry was a platinum minidisc electrode (3×10^{-3} cm²). For electronic spectroscopy a 0.8×2.5 cm indium–tin oxide (ITO) sheet (ca. 80% transmittance, ca 300 Ω/square resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm²) was used in preparative electrolyses.

The voltammetric apparatus for general electrochemical investigation was AMEL (Italy) and included a 551 potentiostat modulated by a 568 programmable function generator coupled to a 731 digital integrator.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra on a Perkin-Elmer 682 spectrometer.

ESR spectra were taken on an X-band ER 100D Bruker spectrometer following the procedure previously described;[18] absolute spin calibration was performed with $VOSO_4 \cdot 5H_2O$ crystals.

Microgravimetric analysis was performed with a gold-coated AT-cut quartz electrode (0.3 cm²), resonating at 6 MHz, onto which the oligomers were deposited. The resonator and the frequency counter were commercial products (Edwards). Calibration of the quartz crystal microbalance was performed with silver deposition and stripping from a 10^{-2} M solution of $AgNO_3$ in 0.1 M TEAP AN.

Results and Discussion

Cyclic Voltammetry. The cyclic voltammograms of thin films of Me_2T_4, Me_2T_6, Me_2T_8, and Me_2T_{10} in 0.1 M TEAP AN, in the potential range 0.0–0.8 V, i.e., the range of stability of PT,[24] are reported in Figure 1 and the relevant peak potentials in Table I.

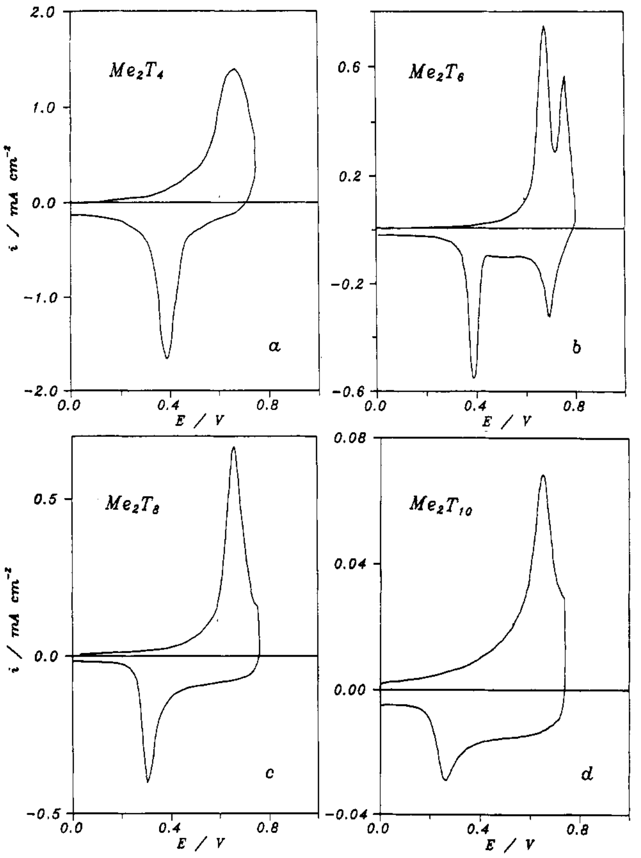

Figure 1. Cyclic voltammogram for (a) tetramer, (b) hexamer, (c) octamer, and (d) decamer deposits in 0.1 M TEAP AN. Scan rate: 0.1 V/s. Q_r = (a) 3 mC/cm²; (b) 1 mC/cm²; (c) 0.9 cm²; (d) 0.1 mC/cm².

Table I. Oxidation (E_p(ox)) and Reduction (E_p(r)) Peak Potentials for Deposits of Me_2T_n in 0.1 M TEAP AN (Scan Rate 0.1 V/s)

n	$E_p(ox)^1$/V	$E_p(r)^1$/V	ΔE_p^1/V	$E_p(ox)^2$/V	$E_p(r)^2$/V	ΔE_p^2/V
4	0.65	0.45	0.20			
6	0.63	0.36	0.27	0.75	0.68	0.07
8	0.67	0.33	0.34			
10	0.64	0.25	0.39			

The tetramer Me_2T_4 (Figure 1a) shows a single reversible cycle, centered around 0.55 V, which involves the reversible formation of the radical cation (1 electron/molecule), as shown by the cyclic voltammogram in DCE solution.[21] Unfortunately with cycling of the potential the response decreases due to the solubility of the radical cation in this medium.

Also the octamer Me_2T_8 (Figure 1c) and the decamer Me_2T_{10} (Figure 1d) show a single reversible cycle centered around 0.5 and 0.45 V, respectively, but at difference the cycle is stable to repetitive cycling. Due to the insolubility of the deposits in any organic solvent, the determination of the electron stoichiometry was made with the quartz crystal microbalance. Thus, deposits up to some micrograms gave a ratio of reversible charge to weight which corresponds to the involvement of 2 electrons/molecule.

The hexamer Me_2T_6 (Figure 1b) is unique in the series as it shows two reversible cycles involving the same charge and centered around 0.5 and 0.72 V. It should be remarked

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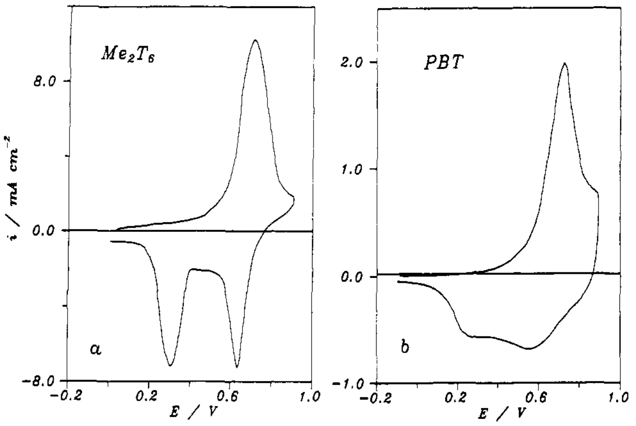

Figure 2. Cyclic voltammogram for electrodeposited (a) hexamer and (b) polybithiophene in 0.1 M TEAP AN. Scan rate: 0.1 V/s; Q_r = (a) 20 mC/cm^2 and (b) 4 mC/cm^2.

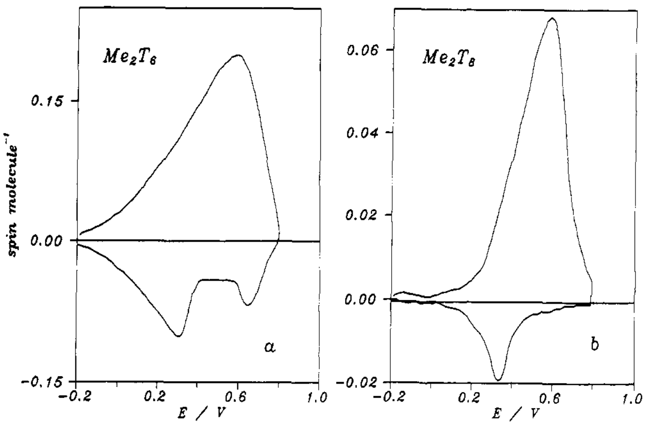

Figure 3. In situ ESR for electrodeposited (a) hexamer and (b) octamer in 0.1 M TEAP AN. Scan rate: 0.05 V/s; Q_r = (a) 5 mC/cm^2 and (b) 1.5 mC/cm^2.

that for thicker deposits the two oxidation peaks merge into one (Figure 2a). Also in this case the response is stable to repetitive cycling. The electron stoichiometry for the redox processes of the hexamer was determined by spectrophotometry, dissolving deposits of known charge content in chlorobenzene and comparing the absorption at l_{max} = 445 nm with that of a sample purified by sublimation. The result is that the overall redox cycle involves also in this case 2 electrons/molecule.

The trend of oxidation in these oligomers, from the one-electron process of the tetramer to the two-electron process of the octamer and decamer through the two subsequent one-electron oxidations of the hexamer is explained by the progressive decrease of the potential separation of subsequent electron transfers already observed in solution for the oxidation of oligothiophenes[6] and the reduction of oligovinylenephenylenes.[25] As observed in the oxidation and reduction of oligophenylenes as thin films,[26] the solid state introduces the phenomenon of hysteresis, e.g., a separation between the forward and backward peak potentials ΔE_p (see Table I). Hysteresis in fact reflects strong attractive interactions among the molecules in the crystals[27] opposing counterion ingress into the structure and is an electrochemical example of the so called unusual quasi-reversibility.[28] This explains both the increased peak separation with the increased length of the oligomer and the lower peak separation for the second oxidative redox process of the hexamer. The former is attributable to an increasingly strong interaction between adjacent molecules while the latter is due to the fact that further accommodation of counterions in an oxidized (open) structure requires a lower threshold energy.

The comparison with PT (from bithiophene in acetonitrile, hereafter called PBT, which yields the best quality polymer[29]) is most surprising as the polymer displays a single oxidation and a twin reverse reduction process quite similar to those of the hexamer (Figure 2b).[18] The surprise arises from the observation that splitting of the redox process in the hexamer, absent in the octamer and decamer, reappears in the polymer. Instead, increasing the chain length is expected to reduce progressively the separation between the redox processes which would finally (in the infinite chain) merge into a single process.[6,25] It is therefore suggested that the fact must be ascribed to some phenomenon which takes place in the solid state.

To understand this anomalous behavior, which constitutes a puzzling aspect of the electrochemistry of polythiophenes, the oligomers have been investigated for their magnetic behavior, in analogy with what has been done with PT,[18] as reported in the next section.

In Situ ESR. For the hexamer (Figure 3a) oxidation produces an ESR signal, which after an initial linear increase with charge, corresponding to the injection of 1 spin/electron, attains a maximum (0.2 spin/molecule) well before the first oxidation peak potential and decreases to zero at complete oxidation. This may be explained with the subsequent formation of the paramagnetic radical cation $Me_2T_6{}^{\bullet+}$ (though the maximum spin concentration is lower than the expected value of 1 spin/molecule) and of the diamagnetic dication $Me_2T_6{}^{2+}$. On the reverse scan the signal reappears with peaks in correspondence with the cyclic voltammetric peaks (0.06 spin/molecule at the transition $Me_2T_6{}^{2+}/Me_2T_6{}^{\bullet+}$ and 0.1 spin/molecule at the transition $Me_2T_6{}^{\bullet+}/Me_2T_6$) and a low-spin plateau (0.04 spin/molecule) in the intermediate potential range. The low value for the one -electron oxidized oligomer must be due to spin pairing, already observed for several radical cations in the solid state,[30] while peaks at the transition potentials may be assigned to the formation of mixed-valence phases in analogy to the results obtained with polymeric tetrathiafulvalene.[31] Though the tetramer could not be investigated in ESR due to its solubility in the oxidized state, it is expected to behave similarly to the hexamer at the first one-electron step, since we previously observed that spin pairing of the radical cation occurs in solution.[21]

For the octamer (Figure 3b) the response, albeit lower, is similar in the oxidative scan, as it goes through a maximum (0.07 spin/molecule) disappearing in the fully oxidized state. The ESR signal reappears in the reverse scan but only in correspondence of the reduction peak, attaining a lower value (0.015 spin/molecule). A similar

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trend is observed for the decamer, with analogously low-intensity values though reliable quantitative data were not obtained due to the difficult deposition of sufficiently thick films. Since an ESR signal is not expected in a direct two-electron oxidation process, it is inferred that the process in fact occurs in two subsequent one electron steps, though the potential separation between them is lower than for the hexamer.

To compare the maximum spin concentrations, in terms of spins per aromatic ring, we considered the data evaluated from the reverse reduction scan, where we may assume that equilibrium conditions are attained as in PBT.[32] It results that the hexamer displays ca. 0.02 spin/ring and the octamer only 0.002 spin/ring. Since for higher oligomers the potential separation between the two one-electron transfers decreases further, paramagnetic species should not form in PT. In fact this conclusion, expected also on the basis of calculations indicating that two polarons are unstable in respect to a bipolaron,[33] is contrary to the experiment which gives a figure of 0.02–0.03 spin/ring in PT[34,35] very close to that of the hexamer. Thus, the similarity between PT and the hexamer, already apparent in cyclic voltammetry, results also in the paramagnetic behavior.

Oligomeric Nature of Polythiophene. We have so far tacitly assumed that PT obtained from bithiophene is a polymer of infinite length. In fact it has been shown that in PT samples, produced from thiophene oxidation at various conditions, the degree of polymerization N_{dp} is rather low, ranging from 10 to 35.[36] It is therefore possible that PBT too is in fact a low-N_{dp} oligomer. By IR measurements of N_{dp} following the method by Furukawa et al.,[3] which is based on the linear relationship of N_{dp} with the inverse of the ratio R of intensity of the bands at 690 and 790 cm^{-1} assigned to the terminal and intrachain thiophene units respectively, we have determined that N_{dp} in PBT is ca. 13. This result is in agreement with the conjugation length N_c evaluated from the optical maximum as follows. The linear relationship of the energy gap (E_g in electronvolts at the maximum absorption) of thiophene oligomers vs the inverse of N_{dp} (in this case N_{dp} and N_c are obviously the same),[37] obtained from oligomers with N_{dp} 2, 3, 4, and 6 in chloroform[38] ($E_g = 3.71/N_c + 2.25$; $r = 0.999\,98$), would allow the determination of N_c for the polymer provided that solid-state and solution spectra are the same. This assumption is not generally true as solvents do cause pronounced hypsochromic shifts (solvatochromism) in alkyl-substituted polythiophenes and eventually with longer alkyl chains.[39] However, the observation that the absorption maxima of Me_2T_6 in chlorobenzene solution and as thin film are almost the same (445 and 450 nm, respectively), which may be due to scarce solvation effects from just two short alkyl groups in a relatively long thiophene chain, suggests that for unsubstituted PT solvation effects are minor. For PBT (maximum absorption at 480 nm) one evaluates a conjugation length oc ca. 11, in good agreement with the IR result, which rules out the intervention of defects (e.g., α–β linkages) during polymerization. Thus, on the basis of IR and electronic spectra, PBT may be roughly assumed as the conjugated dodecamer.

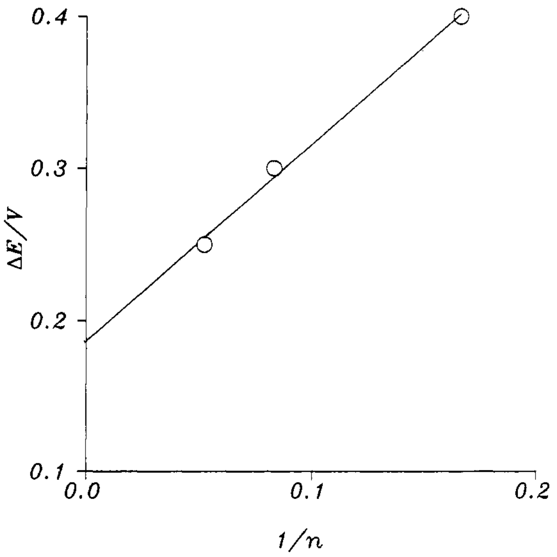

Figure 4. ΔE (cyclovoltammetric peak separation) vs $1/n$ plot for polythiophenes (n = 6, 12, and 19).

Starting from this result the twin redox cycle of PBT could be not a feature of the infinite polymer and may be accounted for in a more simple way. As subsequent redox processes tend to associate in pairs as N_{dp} is increased,[25] the two one-electron processes detectable for the hexamer in the allowed potential range (up to 0.8 V in our medium) may become two couples of closely spaced one-electron processes in the dodecamer (4 electrons/12 rings, i.e., 0.33 electron/ring, are the maximum compatible with the experimental value of one electron per 3–4 monomeric units found also in other conducting polymers such as polypyrrole). In any case merging of redox processes should continue as the polymer chain becomes longer and infinitely long PT would display a single process at lower potentials. This information was gained by extrapolation from other PT oligomers. Polythiophene films obtained from bithiophene in nitrobenzene (4×10^{-2} M bithiophene at 40 °C and j = 0.1 mA/cm^2) display a maximum adsorption at 507 nm indicating a N_c = ca. 19 and its cyclic voltammogram shows the twin process with a more negative average peak potential and lower separation ΔE in comparison with the polymer obtained in acetonitrile (ΔE = 0.25 vs 0.30 V). On the contrary α-sexithienyl films are oxidized at a more positive potential and the peak separation is higher (ΔE = 0.40 V). The ΔE vs $1/n$ plot for the three oligomers (Figure 4) is fairly linear (r = 0.9975) with an intercept of 0.18 V. The nonzero value of the intercept, i.e., of the peak separation in the infinite polymer, conclusively confirms than the twin redox process is not the outcome of a short oligomer but an intrinsic property of the polymer.

Conclusions

The observation of solid-state magnetic dimerization in the hexamer may be the key result for the explanation

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of the twin redox system in PT. From calculations[40,41] as well as IR experiments[2,42] it has been established that in PT the oxidative paramagnetic defect (polaron) extends approximately over six monomeric units. It is therefore conceivable that, in the course of PT oxidation, initially formed hexameric polarons dimerize magnetically forming what we previously called "first bipolaron state";[18] further oxidation to bipolarons takes place only after complete dimerization of hexameric polarons. *The twin electrochemical response of PT is thus the result of the solid-state stabilization of the radical cations (polarons) provided by the magnetic dimerization of hexameric segments.* It must be remarked that this magnetic (or π) dimerization has been recently found also by Hill et al. in end-capped bi- and terthiophenes in solution[10,11,14] and invoked as a possible explanation for the low spin concentration observed in oxidized PT,[10] in full agreement with our conclusions. Also, Diaz et al., from an electrochemical approach different from ours, draw our same conclusions that the two oxidation steps are an inherent property of PT and that they are related to large conjugated segments of the polymer.[8]

A final comment concerns the peculiarity to PT of the twin oxidation process. The reason why this behavior is observed in PT and not in the analogous polypyrrole may be due to the higher tendency of the former to undergo π-dimerization due to a better intermolecular overlapping of the π-electron system.[43] This point is among the objects of our actual investigations.

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