Chem. Mater. **1993,** *5,* 1456-1464

Effects of Substitution of the Median Thiophene Ring on the Electrodeposition and Structure of Poly(terthienyls)

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Received April 15, 1993. Revised Manuscript Received July 12, 1993[●]

α-terthienyls (3Ts) substituted at the β-position of the median thiophene ring by methyl (MTT), octyl (OTT), and dioxaheptyl (DHTT) groups have been sythesized and their electrooxidation and electropolymerization have been investigated with reference to unsubstituted 3T (TT). The electrooxidation process appears strongly dependent on the initial substrate concentration, and the emergence of a concentration-dependent additional oxidation wave between those corresponding to the formation of the cation radical and dication states suggests the occurrence of an aggregation process. Although substitution does not significantly affect the oxidation potential of the 3T system, the nature of the attached substituent strongly affects the electropolymerization process and the structure of the resulting material. The analysis of the electrochemical and optical properties of the various poly(terthienyls) (P3Ts) by cyclic voltammetry and UV-visible absorption spectroscopy shows that the electropolymerization of all 3Ts is accompanied with the trapping of significant amounts of starting material in the film. Although TT leads to a poorly conjugated polymer, the grafting of long alkyl or oxyalkyl chains on the 3T system produces a several hundred millivolts decrease of the oxidation potential of the polymer and a 70-80-nm bathochromic shift of its absorption maximum, changes that are indicative of a considerable extension of conjugation. These results are discussed with regard to the specific reactivity of 3T system and to effects of substitution on the solubility of their electrooxidation products.

Introduction

The remarkable electronic, electrochemical, and optical properties of conjugated poly(thiophenes) (PTs) together with the wide range of their potential technological applications have been the focus of considerable interest over the past decade.[1] Among the various routes adopted for the synthesis of these polymers, electrochemical polymerization has retained special attention.[2] As a matter of fact, the direct electrodeposition of a conducting material onto an electrode surface constitutes a method of choice for the realization of modified electrodes by electropolymerization of monomers derivatized by functional groups with specific activity.[3] On the other hand, electropolymerization, which has been shown to lead to the most conjugated and hence most conducting PTs,[4] can also produce particular structures such as helical PT chains.[5] In this context, several works have been devoted to the analysis of the electropolymerization process in order to achieve a better control of the structure and properties of PTs.[1,2,4,6] Since the formation of α–β' linkages during chain extension still constitutes one of the major problems in thiophenes polymerization, a possible answer to this question involves the modification of the monomer structure. Thus, substitution of the β–β' positions[7] or, in contrast, activation of the α–α' ones[8] can contribute to improve the stereoregularity of the polymer. Another strategy has also been proposed which consists in using an α-conjugated thiophene oligomer (nT) as starting material for electropolymerization. As a matter of fact, since these substrates contain exclusively α–α' linkages, a statistical

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[●] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

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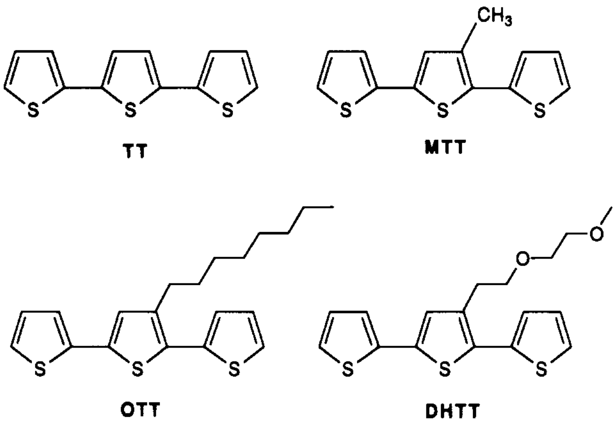
Chart I



decrease of the number of α–β' coupling in the resulting polymer could a priori be expected.[9] However, until now the demonstration of the validity of this approach is still to be made, and experimental works have shown that, contrary to the expected result, electropolymerization of nTs produces less conjugated polymers containing considerable amounts of short-chain oligomers.[10] This phenomenon can be explained by two main causes. On one hand, the delocalization of the positive charge over the entire nT molecule results in a drop of the overall reactivity of the cation radical.[11] On the other hand, the solubility of nTs which decreases rapidly with chain length, is subject to a further dramatic decrease upon oxidation to cationic forms, leading to their precipitation onto the electrode as soon as a few couplings have occurred. These processes can account for the presence of large amounts of sexithienyl (6T) and terthienyl (TT) in the material resulting from the electropolymerization of TT[10,12] and for the fact that electrooxidation of some substituted 6Ts can lead in some cases to the precipitation of their dication salts.[13]

As a part of a program aimed at the development of new substituted nTs,[13,14] we report here the synthesis and electrochemical behavior of a series of terthienyls (3Ts) substituted at the β-position of the median thiophene ring by methyl (MTT), octyl (OTT) and dioxaheptyl (DHTT) groups (Chart I).

These substituents have been selected on the basis of their well-known effects on the solubility and environmental sensitivity of β-substituted PTs.[1,4,15] Furthermore, their grafting on the median thiophene ring allows the analysis of their effects on the electrooxidation of the π-conjugated 3T system and on the structure and properties of the resulting materials without the complications arising from the steric interactions associated with β-substitution of the end thiophene rings.[16] The analysis of the electrooxidation of these compounds and the characterization of the electrochemical and optical properties of the resulting materials shows that, despite their moderate and rather similar $+I$ effects, these substituents induce considerable differences in the electropolymerization of the various 3Ts and in the structure and properties of the resulting polymers.

Experimental Section

Thiophene, 3-methylthiophene, 3-bromothiophene, 2,5-dibromothiophene, and 2-(3-thienylethanol) (Aldrich) were used as received. 3-Octylthiophene was prepared by coupling of 3-bromothiophene with octylmagnesium bromide in the presence of bis(diphenylphosphino)–1,3–propanenickel(II) chloride (NiDPPPCl$_2$).[17] 3-(3,6-dioxaheptyl)thiophene was obtained by coupling of 2-(3-thienylethanol) and 2-chloroethyl methyl ether.[18] Bromination of the various monomers using Br$_2$ in CHCl$_3$ at room temperature afforded the 2,5-dibromothiophene derivatives. The four 3Ts were then obtained in 60–90% yield by coupling 2-thienylmagnesium bromide with the appropriate 2,5-dibromothiophene in the presence of NiDPPPCl$_2$.

Electrochemistry was performed with a PAR 273 potentiostat–galvanostat, in a three-electrode single-compartment cell equipped with platinum microelectrodes of 7.85×10^{-3} cm^2 area, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Electrooxidations and electropolymerizations were carried out in MeCN solutions (HPLC grade) containing 0.1 M tetrabutylammonium perchlorate (Fluka puriss) and the 3Ts at concentrations of 5×10^{-4}, 5×10^{-3}, and 5×10^{-2} M. Solutions were degassed by nitrogen bubbling prior to each experiment which was run under a nitrogen atmosphere. Films for electrochemical characterization were deposited in potentiostatic conditions at the first oxidation potential of the 3T, using a deposition charge of 50 mC cm^{-2}. The polymer films were then rinsed with hexane and placed in another cell containing 0.1 M Bu$_4$NClO$_4$ in MeCN. Films for optical characterization were grown in galvanostatic conditions (typically 2 mA cm^{-2}) on optically transparent indiumtin oxide (ITO) electrodes and electrochemically undoped. In spite of the use of a same deposition charge of 50 mC cm^{-2} for all the poly(terthienyls) (P3Ts), the partial solubility of the deposits due to the presence of oligomeric species, and their limited cohesion produced rather large variations in the optical densities of the various films. UV–visible absorption spectra were recorded on a Lambda 2 Perkin-Elmer spectrometer.

Results and Discussion

Electrooxidation of 3Ts. Due to the presence of free α-positions, the cations radicals resulting from the electrooxidation of 3Ts are subject to subsequent chemical coupling. This irreversible process renders the precise determination of the redox potentials of the 3Ts cation radical and dication difficult. However, the use of low substrate concentration and high scan rates allows the observation of the successive oxidation processes associated with the formation of these two cationic species. Figure 1 shows the single-scan voltammograms recorded in MeCN solutions containing increasing TT concentrations (C). The CV recorded with $C = 5 \times 10^{-4}$ M exhibits an anodic peak

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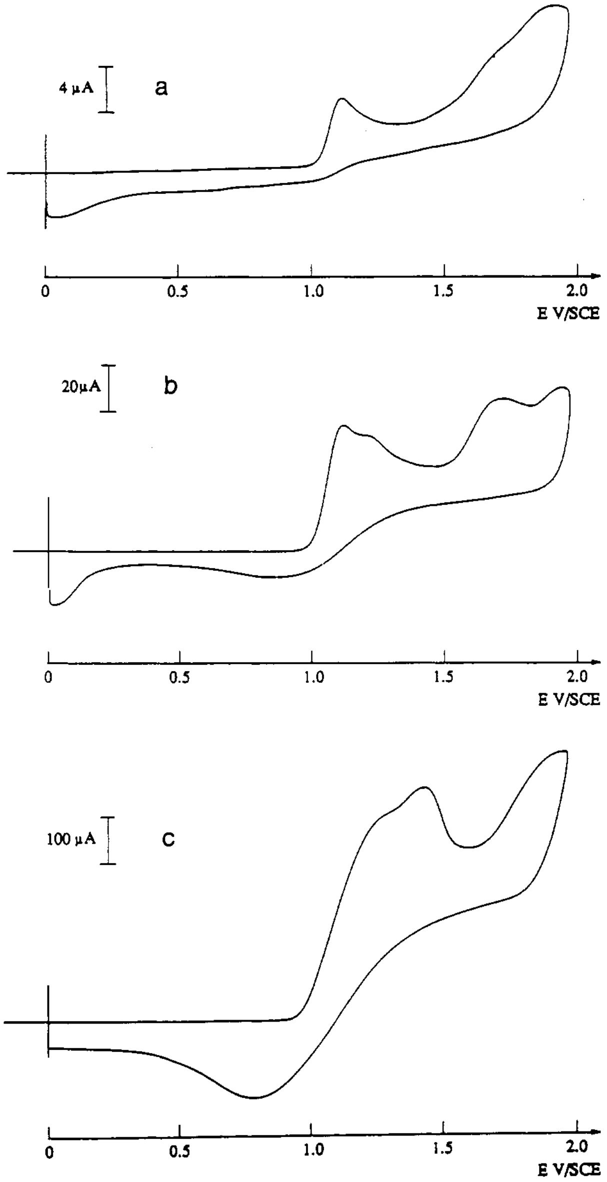

Figure 1. Single-scan cyclic voltammograms of TT in 0.1 M Bu_4NClO_4–MeCN, scan rate 300 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-3}$ M, (c) $C = 5 \times 10^{-2}$ M.

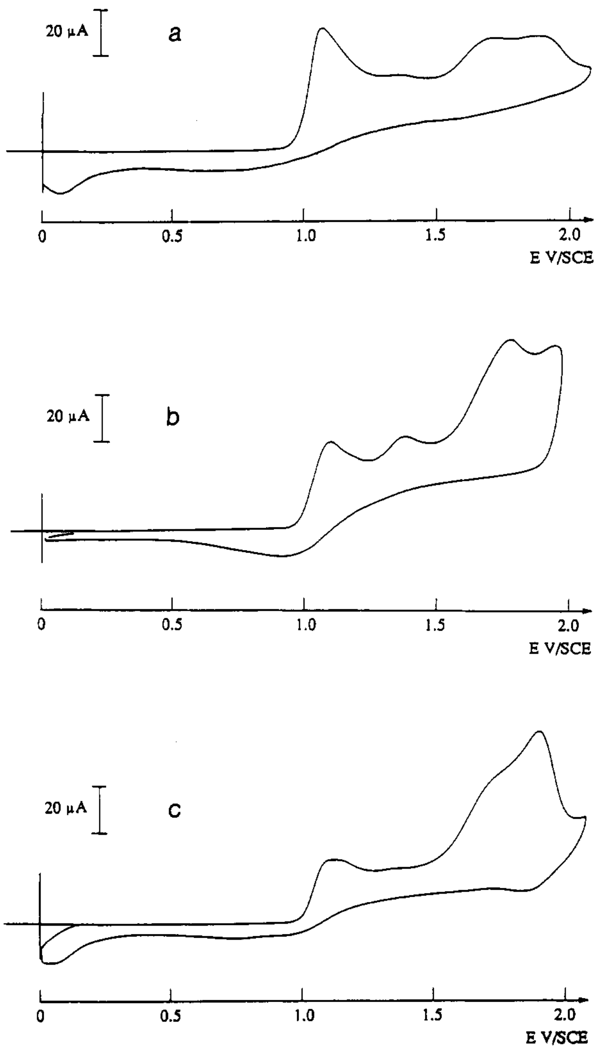

Figure 2. Single-scan cyclic voltammograms of 3Ts in 0.1 M Bu_4NClO_4–MeCN, scan rate 300 mV s^{-1}. (a) MTT, (b) OTT, (c) DHTT.

(Epa1) at 1.07 V followed by a broad wave involving two components at 1.65 and 1.90 V (Figure 1a). Although, as could be expected, none of these waves is reversible, Epa1 can be unequivocally assigned to the formation of the cation radical $TT^{\bullet+}$. The oxidation wave corresponding to the formation of the dication state is more difficult to ascertain, however, comparison with the data reported for end-substituted 3Ts[19] suggests that this process corresponds to the 1.65 V shoulder (Epa2), whereas the wave in the 1.90-V region can be ascribed to the degradation of the molecule. Increasing C to 5×10^{-3} M improves the resolution of both the 1.07- and 1.65-V waves while a new wave emerges at 1.17 V (Epa3, Figure 1b). Concurrently the weak cathodic wave appearing in the cathodic scan indicates that electrodeposition has started during the positive scan. A further increase of C to 5×10^{-2} M considerably enhances the rate of electrodeposition as shown by the intensification of the cathodic wave (Figure 1c) and by the appearance of a black deposit on the electrode. Despite the loss of resolution and positive shift of the CV waves caused by the superimposition of the electrodeposition process to the oxidation of solution species, comparison of the CV recorded with $C = 5 \times 10^{-2}$ M with those of Figure 1a,b shows that the new anodic wave at 1.37 V has now become predominant. The dependence of the intensity of this new wave on substrate concentration strongly suggests the occurrence of an aggregation process. The appearance of additional CV waves caused by aggregation has already been observed in the case of polystyrene–tetrathiafulvalene electroactive polymers.[20] More recently, spectroelectrochemical studies on stable cation radicals derived from end-substituted nTs have led to the proposal of cation radical π-dimers $(TT)_2^{\bullet+}$.[21] On the basis of these findings, it can be proposed that Epa3 corresponds to the oxidation of $(TT)_2^{\bullet+}$ to the dimer dication $(TT)_2^{2+}$.

Figure 2a–c shows the CVs recorded in 5×10^{-3} M solutions of the substituted 3Ts. These curves and the data in Table I show that Epa1 and Epa2 values are rather similar to those of TT with perhaps a slight anodic shift

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Table I. Cyclic Voltammetric Data for 3Ts[a]

3T	concn (M)	Epa1 (V)	Epa2 (V)	Epa3 (V)
TT	5×10^{-4}	1.07	1.63	
TT	5×10^{-3}	1.07	1.65	1.17
TT	5×10^{-2}	1.20		1.37
MTT	5×10^{-3}	1.03	1.64	1.30
OTT	5×10^{-3}	1.05	1.70	1.32
DHTT	5×10^{-3}	1.05	1.65	1.29

[a] Measured at 300 mV s^{-1} in 0.1 M Bu_4NClO_4–MeCN. All potentials in V/SCE.

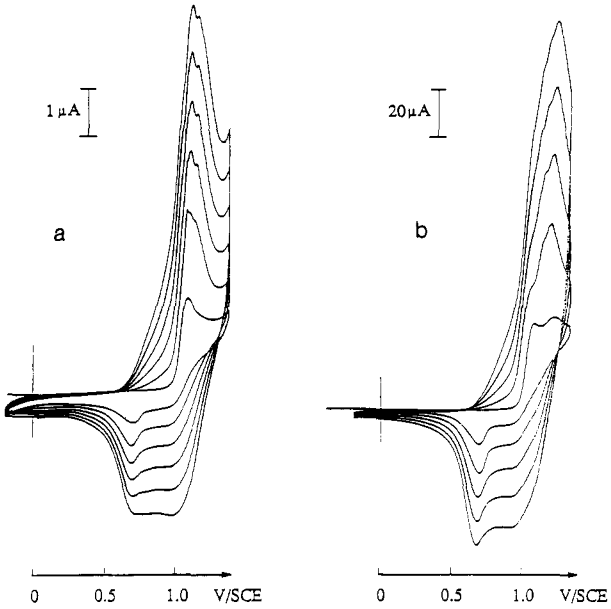

Figure 3. First cyclic voltammograms corresponding to the electrodeposition of poly(TT) by recurrent potential scans between −0.2 and +1.25 V. Electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 100 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-3}$ M.

of Epa1 which could be related to the weak +*I* effect of alkyl substituents. In contrast, Epa3 occurs at ca. 1.30 V instead of 1.17 V for TT. This anodic shift suggests that intermolecular steric interactions can induce changes in the structure of the π-dimer cation.

Electropolymerization of 3Ts. Figure 3 and 4 show the CVs obtained by successive potential scans in MeCN solutions containing 5×10^{-4} and 5×10^{-3} M TT. As for single-scan voltammetry, the first CV trace in Figure 3a shows two anodic subpeaks in the potential region corresponding to the formation of the cation radical. Interestingly, the CVs recorded with $C = 5 \times 10^{-3}$ M (Figure 3b) shows that the inversion of the relative intensity of the 1.07- and 1.17-V peaks, previously observed when increasing *C* to 5×10^{-2} M TT (Figure 1c) occurs here during the second scan, i.e., after material deposition has already started during the first scan. Taking into account the concentration dependence of aggregation processes, this result suggests that the deposited material also contains the π-dimer cation. Repetitive cycling produces the emergence of a cathodic peak at 0.70 V related to the reduction of the deposited material while a broad anodic shoulder corresponding to its oxidation develops in the 0.50–1.00-V region (Figure 4). Since the anodic potential is limited to the first oxidation potential of TT, this result confirms that electrodeposition occurs via the cation radical state. Although increasing *C* increases the electrodeposition rate, as shown by the larger current scales of Figures 3b and 4b, the overall shape of the CV is not significantly affected except for a slight loss of resolution related to the increase of film thickness.

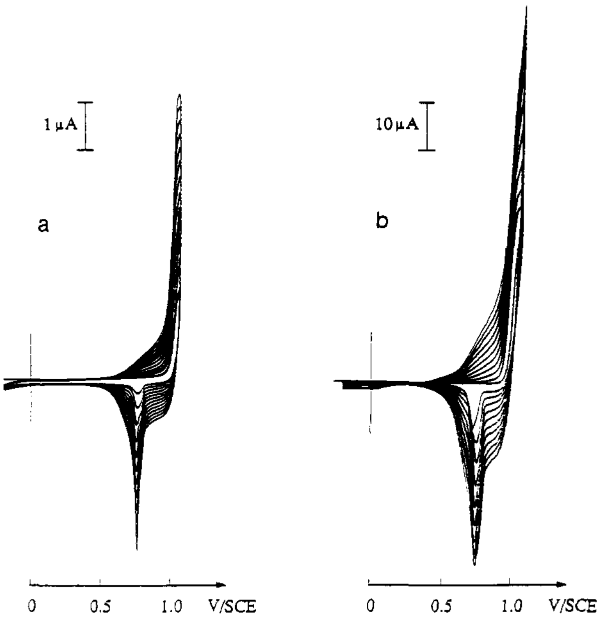

Figure 4. Electrodeposition of poly(TT) by recurrent potential scans between −0.2 and +1.05 V. Electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 100 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-3}$ M.

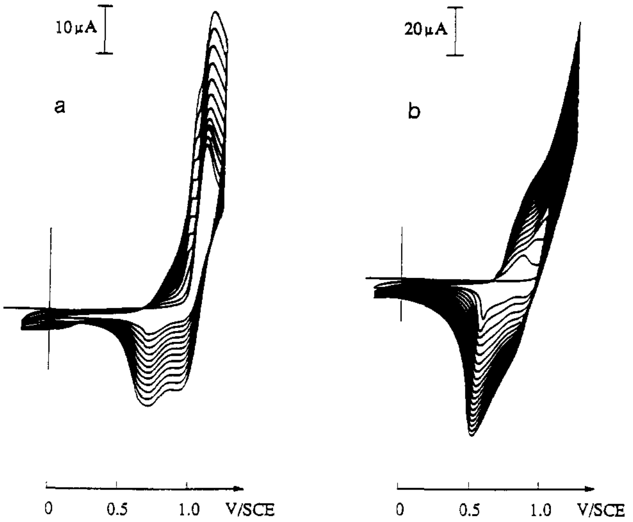

Figure 5. Electrodeposition of poly(MTT) by recurrent potential scans between −0.2 and +1.05 V. Electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 100 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-3}$ M.

Figures 5 and 6 show the multisweep CVs recorded with two concentrations of MTT and OTT. Unlike TT, the increase of *C* produces a dramatic loss of the waves resolution. However, the CVs recorded with $C = 5\ 10^{-4}$ M (Figures 5a and 6a) show that instead of the broadening of the main anodic wave observed with TT, electrodeposition of MTT and OTT leads to the emergence of a new oxidation wave at lower potentials. This phenomenon is particularly evident with OTT for which, a symmetrical well-defined new redox system with a sharp anodic peak at 0.80 V progressively develops (Figure 6a).

As shown in Figure 7, electrodeposition of DHTT results also in the emergence of a new redox system with a further cathodic shift of the new anodic peak to 0.72 V. However, contrary to the previous cases, the increase of *C* to 5×10^{-2}

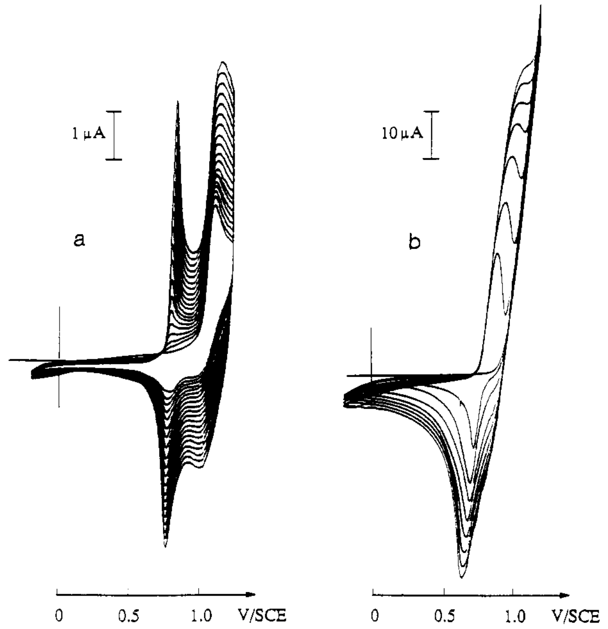

Figure 6. Electrodeposition of poly(OTT) by recurrent potential scans between −0.2 and +1.05 V. Electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 100 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-3}$ M.

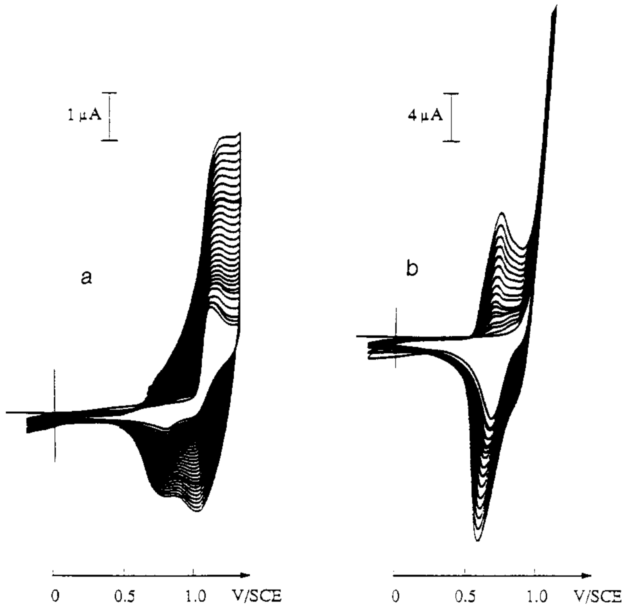

Figure 7. Electrodeposition of poly(DHTT) by recurrent potential scans between −0.2 and +1.05 V. Electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 100 mV s^{-1}. (a) $C = 5 \times 10^{-4}$ M, (b) $C = 5 \times 10^{-2}$ M.

M greatly improves the definition of the CV. Although the interpretation of this quite different behavior is not straightforward, it is strongly reminiscent of the electropolymerization of thiophenes containing oligoxyethylene substituents. As a matter of fact, it has been observed that electrodeposition of these PTs requires higher monomer concentrations and current densities than electropolymerization of 3-alkylthiophenes. Furthermore, the increase of the number of oligoxyethylene groups leads progressively to a complete inhibition of electropolymerization.[22]

To summarize, the comparison of the electropolymerization CVs of the various 3Ts with their single scan CVs shows that although alkyl and oxyalkyl substituents have no or little effect on the oxidation potential of the 3T system, they considerably affect the electropolymerization process.

Cyclic Voltammetry of P3Ts. To gain more detailed informations on the specific effects of the various substituents on the electrochemical properties of P3Ts, the cyclic voltammetric response of thin films potentiostatically deposited on Pt microelectrodes has been analyzed. As already reported, the CV of a poly(terthienyl) (PTT) film deposited from a 5×10^{-3} M TT solution (not shown) exhibits a well resolved anodic wave with Epa at 1.09 V and a cathodic wave involving a broad shoulder at ca. 1.00 V and a reduction peak at 0.67 V.[10a] However, increasing scan rate produces a broadening of the anodic wave, which suggests the presence of two subcomponents. This hypothesis is confirmed by the CV of the film deposited with lower TT concentrations. As a matter of fact, decreasing C leads to a decrease of the faradaic yield of electrodeposition and hence of film thickness. As a consequence of the enhanced resolution associated with the reduction of film thickness,[4] two anodic subpeaks at 1.02 and 1.08 V can be distinguished in the CV of the PTT film obtained with $C = 5 \times 10^{-4}$ M (Figure 8a). The similarity of these peaks with those already observed in solution (Figure 1), or during film deposition (Figure 3), indicates that the already detected π-dimers are also present in the polymer film.

Figure 8b shows the first CV recorded over a wider potential range (−0.2 to +1.35 V). Owing to the rapid degradation of the film at highly anodic potentials, a stable wide-range cyclic voltammogram (WRCV) could not be obtain. However, the recording of the first WRCV allows the observation of a second well-defined redox system with Epa at 1.23 V. Previous works have shown that electropolymerization of TT results in the trapping of significant amounts of TT in the film.[10,12] These findings suggest that the second anodic wave at 1.23 V corresponds to the oxidation of the TT molecules trapped in the film. The apparent reversibility of this redox system is in striking contrast with the irreversible waves observed in homogeneous liquid media (Figure 1). This apparent contradiction can be explained by immobilization of the trapped TT molecules in the deposited material, which limits the rate of chemical coupling of $TT^{\bullet+}$. However, repetitive cycling results in the rapid disappearance of this second system and to an anodic shift of the first one due to the coupling of the trapped $TT^{\bullet+}$[10b] and to the overoxidation of the long conjugated segments at highly anodic potentials.[23]

Although a similar general behavior is observed with substituted P3Ts, substitution of the central thiophene ring induces noticeable differences in the electrochemical properties of the deposited materials. The WRCV of PMTT exhibits a sharp first anodic peak at 0.86 V followed by a broad wave with Epa2 at 1.12 V whereas the reverse scan involves two broad cathodic waves with Epc2 and Epc1 at 0.97 and 0.67 V (Figure 9b). Limiting the potential range to the first redox system improves the resolution of the CV and leads to cathodic shift of Epa1 from 0.86 to

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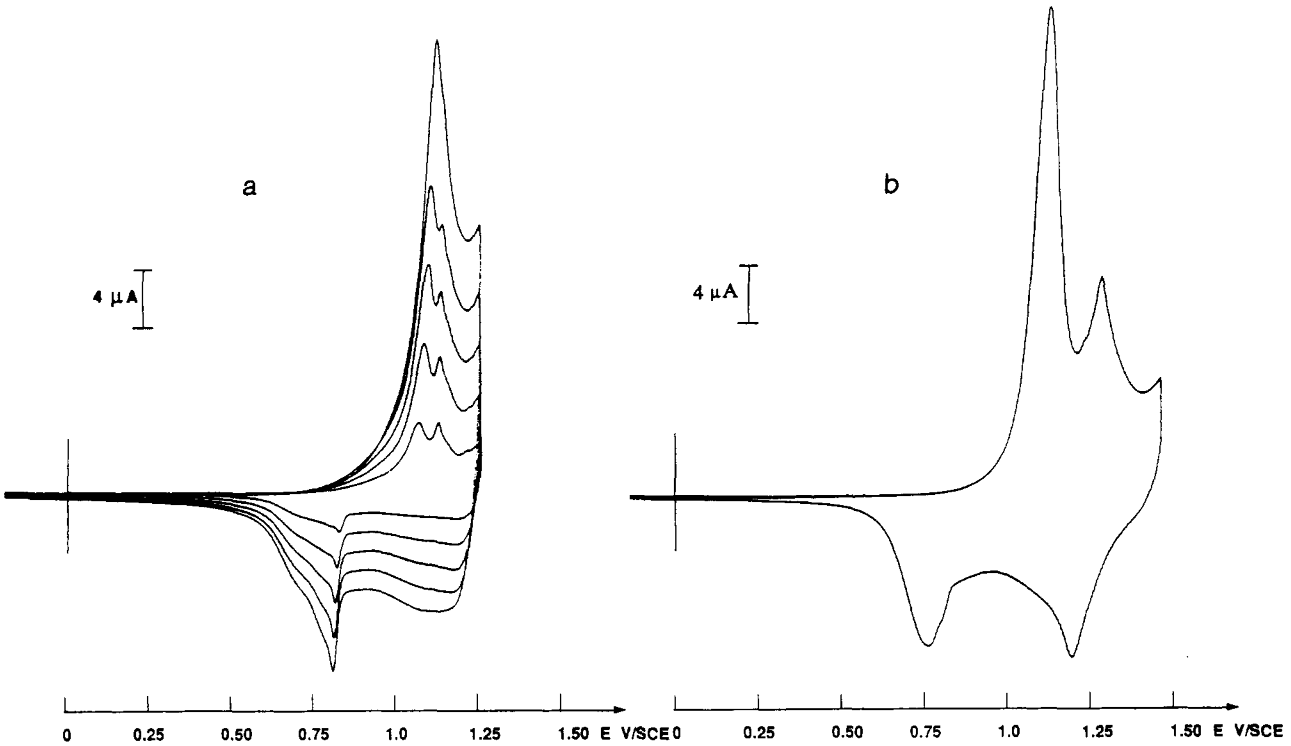

Figure 8. (a) Cyclic voltammograms of poly(TT) prepared with $C = 5 \times 10^{-4}$ M. Qd = 50 mC cm^{-2}. Potential limits: −0.20 to +1.20 V, electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 20–100 mV s^{-1} by increment of 20 mV s^{-1}. (b) First cycle up to 1.40 V, scan rate 100 mV s^{-1}.

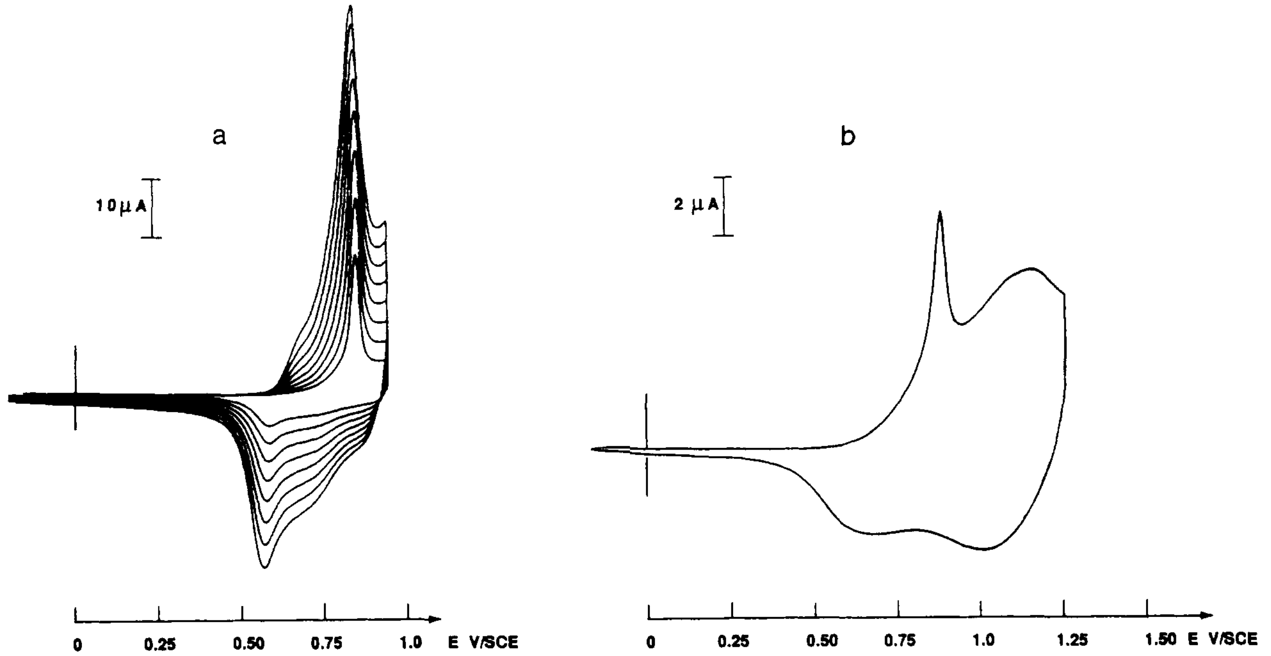

Figure 9. (a) Cyclic voltammograms of poly(MTT) prepared with $C = 5 \times 10^{-3}$ M. Qd = 50 mC cm^{-2}. Potential limits: −0.20 to +0.90 V, electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 40–180 mV s^{-1} by increment of 20 mV s^{-1}. (b) Film prepared with $C = 5 \times 10^{-4}$ M, first cycle up to 1.20 V, scan rate 60 mV s^{-1}.

0.80 V and to the appearance of a new sharp peak at 0.54 V in cathodic wave (Figure 9a).

Although the WRCV of POTT also exhibits two successive redox systems (Figure 10b), a further cathodic shift of Epa1 to 0.68 V occurs (Table II). As shown by the CV of the first system, this decrease of the oxidation potential is accompanied with a considerable increase of the symmetry of the CV waves (Figure 10a). The high resolution of this CV, and the fact that the width at half-maximum of the anodic peak is close to the 90 mV expected for a surface reaction with ideal Nernstian behavior strongly suggests the oxidation of a single species with a defined conjugation length.[24]

As could be expected from electrodeposition curves, the best resolved CVs of PDHTT are obtained with the films prepared with the highest DHTT concentration. As for other P3Ts, two distinct redox systems are observed in

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(24) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamental and Applications*; Wiley: New York, 1980.

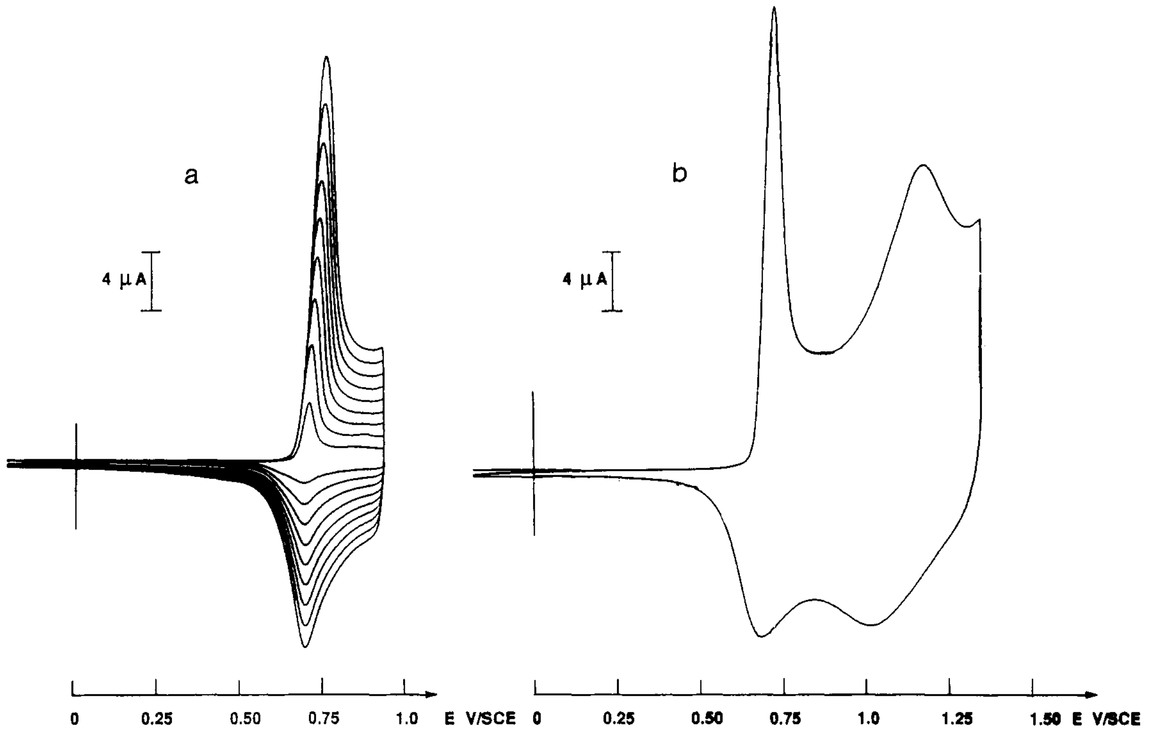

Figure 10. (a) Cyclic voltammograms of poly(OTT) prepared with $C = 5 \times 10^{-3}$ M. Qd = 50 mC cm^{-2}. Potential limits: −0.20 to +0.90 V, electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 20–180 mV s^{-1} by increment of 20 mV s^{-1}. (b) First cycle up to 1.30 V, scan rate 180 mV s^{-1}.

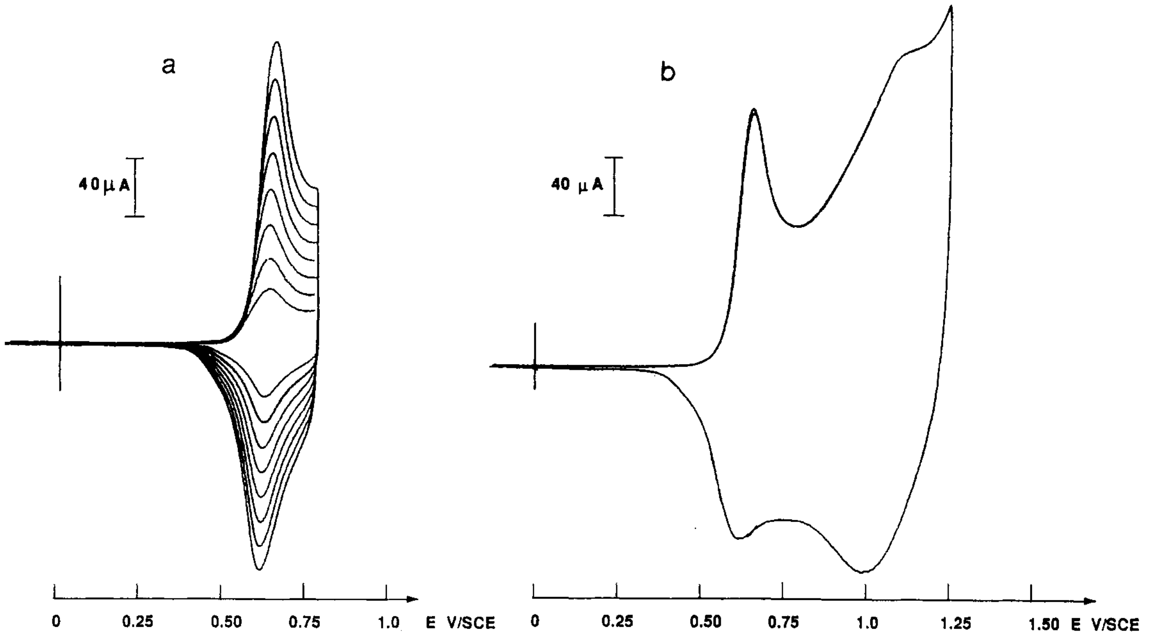

Figure 11. (a) Cyclic voltammograms of poly(DHTT) prepared with $C = 5 \times 10^{-2}$ M. Qd = 50 mC cm^{-2}. Potential limits: −0.20 to +0.75 V, electrolytic medium: 0.1 M Bu_4NClO_4–MeCN, scan rate 40–180 mV s^{-1} by increment of 20 mV s^{-1}. (b) First cycle up to 1.20 V, scan rate 180 mV s^{-1}.

the WRCV (Figure 11b). However, whereas Epa2 remains in the 1.10-V region, a further cathodic shift of Epa1 to 0.60 V occurs together with an improvement of the symmetry of the CV (Figure 11a).

The CVs of the various P3Ts and the data in Table II show that substitution of TT by long alkyl or oxyalkyl chains leads to an improvement of the resolution and symmetry of the CV of the first redox system and to a considerable cathodic shift of Epa1 (420 mV from PTT to PDHTT). These results suggest that the grafting of substituents of increasing length and solubilizing power on the 3T system allows the formation of considerably more conjugated polymer chains than TT itself. In contrast, the fact that the nature of the attached sub-

Table II. Cyclic Voltammetric Data for Poly(3Ts) Electrodeposited on Pt. Electrolytic Medium 0.1 M Bu_4NClO_4–MeCN[a]

poly(3T)	Epa1 (V)	Epa2 (V)	Epa1 (V)[b]
poly(TT)	1.09	1.24	1.02
poly(MTT)	0.85	1.12	0.80
poly(OTT)	0.70	1.13	0.68
poly(DHTT)	0.61	1.05	0.60

[a] Scan rate 60 mV s^{-1}, deposition charge (Qd = 50 mC cm^{-2}).
[b] Determined on the CV of the first system.

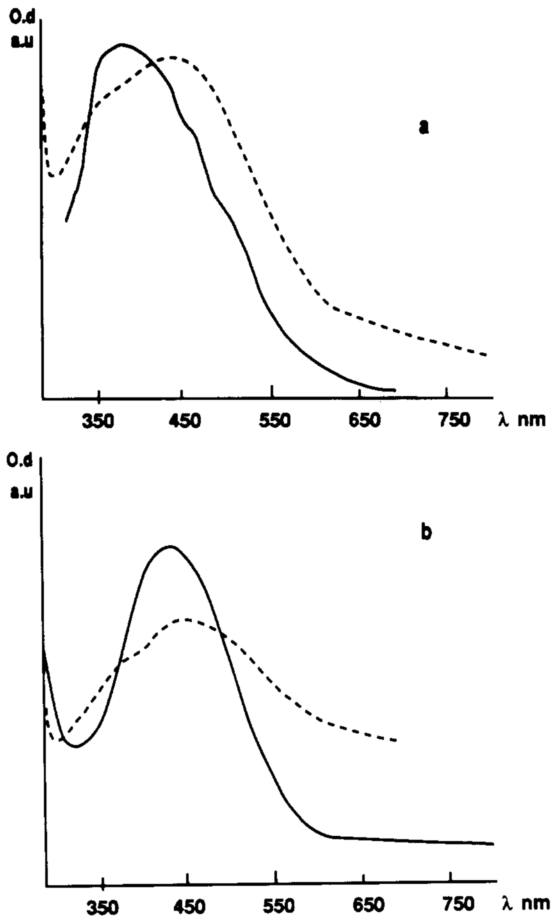

Figure 12. Electronic absorption spectra of undoped poly(3Ts) deposited on ITO using 2 mA cm^{-2}, Qd = 50 mC cm^{-2}. (a) Solid line PTT, dotted line PMTT. (b) Solid line POTT, dotted line PDHTT.

Table III. UV-Visible Spectroscopic Data for 3Ts (4.5 × 10^{-3} M in MeCN) and P3Ts (Qd = 50 mC cm^{-2} on ITO)

3T	λ_{max} 3T (nm)	ϵ_{max} 3T (10^4)	λ_{max} Poly(3T) (nm)
TT	351	2.09	380
MTT	348	2.08	448
OTT	338	1.71	450
DHTT	342	1.41	463

stituent does not affect the potential of the second redox system which remains close to the first oxidation potential of the 3T precursor, suggests that the second anodic wave corresponds to the oxidation of substrate molecules trapped in the film.

UV-Visible Absorption Spectroscopy. To complete these observations, the effects of substitution on the electronic spectral features of both the starting 3Ts and the resulting P3Ts have been analyzed. As shown by the UV-visible absorption data listed in Table III, the introduction of substitutents of increasing size on the median thiophene ring leads to a progressive hypsochromic shift of the absorption maximum together with a decrease of the absorption coefficient. This result suggests a progressive departure from planarity caused by the steric hindrance resulting from the substitution of the central thiophene ring.

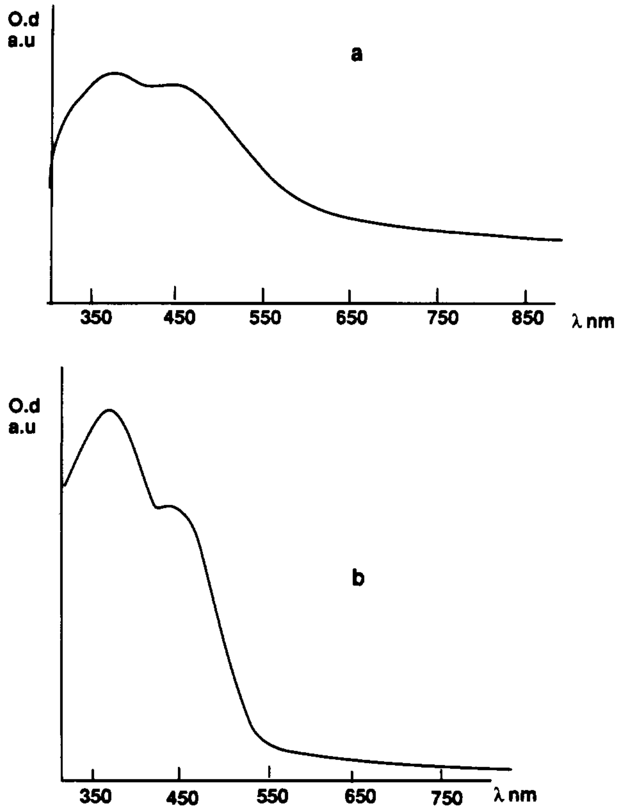

Figure 13. Electronic absorption spectra of undoped poly(3Ts) deposited on ITO using 0.2 mA cm^{-2}, Qd = 50 mC cm^{-2}. (a) PMTT, (b) POTT.

Figure 12 shows the absorption spectra of neutral polymer films electrodeposited on optically transparent electrodes. As already reported, the spectrum of PTT shows a broad maximum around 380 nm followed by a succession of shoulders.[10a] On the other hand, the spectra of substituted polymers, reveal a bathochromic shift of λ_{max} to 448, 450, and 463 nm for PMTT, POTT, and PDHTT, respectively. These results confirm, in agreement with electrochemical data, that substitution of the median thiophene ring of TT allows the formation of more conjugated polymers than TT itself. A further examination of the spectra of PMTT and PDHTT (Figure 12) shows that an additional shoulder occurs in the 350–70-nm region. The similarity of this wavelength with the λ_{max} of the 3Ts suggests that this shoulder corresponds to the starting 3T trapped in the film. To test this hypothesis, films of PMTT and POTT have been deposited using very low current densities which are known to enhance oligomers formation.[4,12] The comparison of the spectra of the films prepared in these conditions (Figure 13) with the previous ones clearly shows a strong increase of the intensity of the 360–70-nm band to the detriment of the low-energy one, thus providing definitive confirmation of the presence the starting 3T in the electrodeposited polymers.

To summarize, although the substitution of the median thiophene ring does not affect the oxidation potential of the 3T system, both the CVs and the electronic absorption spectra clearly show that substituted P3Ts are significantly more conjugated than PTT. A possible explanation for this apparent paradox could resort to the increased solubility that the grafting of long alkyl or oxyalkyl chains provides to the oligomers resulting from the chemical coupling of the 3Ts cation radicals. Similarly to the electropolymerization of five-member heterocycles,[2,11,25] the first step in the growth of a poly(3T) chain consists

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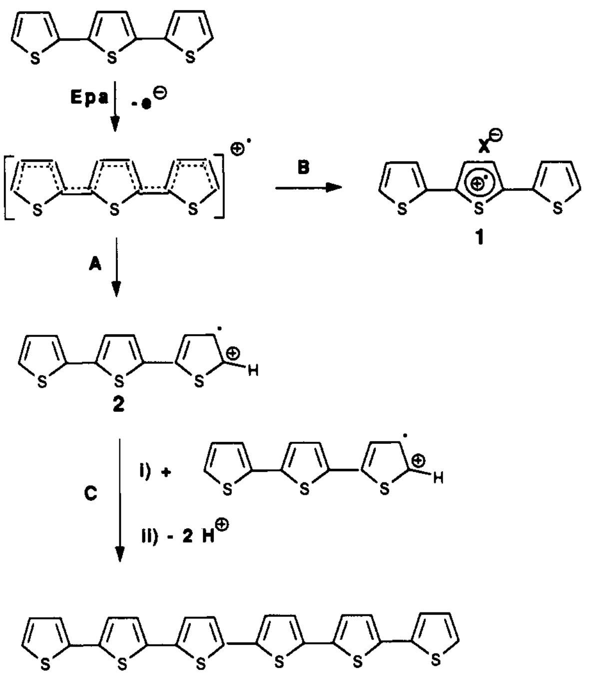
(25) Genies, E. M.; Bidan, G.; Diaz, A. F. *J. Electroanal. Chem.* **1983**, *149*, 101.

Scheme I



in the chemical coupling of the electrogenerated 3T cations radicals. In the case of TT, this process leads to 6T which, due to the applied potential, occurs in its oxidized form, i.e., cation radical or dication. Since neutral 6T already is almost insoluble, oxidation leads to a further decrease of solubility which provokes the precipitation of the oxidized 6T onto the electrode surface, thus limiting subsequent chain growth. In contrast, the enhanced solubility of substituted 3Ts allows further couplings of $3T^{\bullet+}$ to occur before the precipitation threshold of the oxidized oligomer, thus allowing the formation of more conjugated polymer chains.

The presence of significant amounts of starting 3T in each poly(3T) is more difficult to explain. As a matter of fact, two mechanisms can be considered. The first involves a simple trapping of solution 3T during film deposition. In this case, the amount of trapped 3T should steadily increase with the 3T concentration used for film deposition. Although this process cannot be neglected, no clear correlation between the relative intensity of the second redox systems in WRCVs and the initial 3T concentration in the electrosynthesis medium was observed. This absence of dependence on substrate concentration suggests that the trapping process could be related to the specific reactivity of the 3T system. As discussed in a recent paper, upon oxidation of a 3T molecule one electron can be removed from either the central thiophene or from one of the end thiophene rings. Consequently, at a given instant, only the cation radical with a positive charge localized at one end of the molecule can contribute to the chain growth (Scheme I, steps A and C). Thus, if a monomeric cation radical has a coupling probability of 1, this probability decreases to $^2/_3$ for $3T^{\bullet+}$.[26] These considerations imply that, as one-third of the formed cation radicals cannot undergo further coupling, they must remain trapped in the polymer as cation radical salts in which the localization of the positive charge in the vicinity of the charge-compensating counter-anion (Scheme I, step B) definitively prevents further coupling.

It is noteworthy that such a mechanism is consistent not only with our results, but also with the increase of the conjugation length observed when an as grown PTT film is cycled in a blank solution.[10b] As a matter of fact, the application of a cathodic potential scan to an oxidized PTT film leads to the reduction of the trapped TT cation radical salt and to the expulsion of the counter anion. This process results in a reinitialization of the whole electroactive system, confering again to the 3T molecules initially trapped as cation radical salts a probability of $^2/_3$ to undergo further coupling. Consequently, repetition of this process over a few redox cycles will finally lead to the complete comsumption of the trapped 3T.

Conclusion

New terthienyls substituted at the β-position of the median thiophene ring have been synthesized. The analysis of their electrooxidation at various substrate concentrations has provided evidence for the appearance of a concentration-dependent additional oxidation wave which suggests the formation of π-dimers in concentrated solutions. Although substitution does not significantly affects the oxidation potential of the 3T system, it exerts considerable effects on the electropolymerization process leading in the case of long alkyl and oxyalkyl chains to the emergence of a new well-defined redox system at low potentials. The analysis of the electrochemical behavior of the resulting polymers has shown that substitution of TT by long alkyl or oxyalkyl chains leads to a significant decrease of the oxidation potential of the polymer. These results together with the correlated bathochromic shift of the absorption maximum show that the grafting of solubilizing substituents on the 3T system allows the electrodeposition of more extensively conjugated polymers than unsubstituted TT. On the other hand, the electrochemical and spectroscopic properties of the various polymers have confirmed the trapping of significant amounts of starting 3T in the as-grown polymers. The fact that this process appears independent of substitution and substrate concentration suggests that it is inherent to the specific reactivity of oligomeric cation radicals.

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(26) Wei, Y.; Chan, C. C.; Tian, J.; Jang, G. W.; Hsueh, K. F. *Chem. Mater.* **1991**, *3*, 888.