

A comparative study of isomeric polydialkylterthiophenes with regular regiochemistry of substitution. Electrochemical synthesis

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Abstract

In this paper is presented the study of electrodeposited polyterthiophenes with regular regiochemistry of substitution. The starting monomers were 3',4' and 3,3''-didodecyl 2,2':5',2'' terthiophene. The presence of long alkyl chains improved the easiness of processability on the resulting polymers. Moreover, the symmetric structure of the monomers allowed a regular regiochemistry of substitution in the resulting polymers. Poly-didodecyl terthiophenes were electrochemically prepared from a mixture of acetonitrile and benzonitrile and then characterized with infrared spectroscopy, mass spectrometry, profilometry and scanning electron microscopy. Formal oxidation potential E° and dimerization rate constants were determined for both monomers by means of ultrafast cyclic voltammetry (scan rate $>5000 \text{ V s}^{-1}$). The comparison of the results revealed the influence of substitution patterns in the determination of the polymerization degree and the kinetic of polymer growth during the electrochemical polymerization. The role of the monomers reactivities was then pointed out in the electrochemical synthesis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Regioregular polyalkylterthiophenes; Electropolymerization

1. Introduction

The attachment of alkyl substituents to the skeleton of conducting polymers represents the most common procedure for the enhancement of solubility and processability in this class of compounds [1–5]. In fact the substitution with long alkyl chains can bring some disadvantages. These are the weakening of π -conjugation induced by the lack of coplanarity between adjacent rings, and the "dilution" of the electroactive segments [6]. In order to minimize the deleterious effects due to the presence of alkyl chains, the synthesis of conducting polymers with regioregular patterns of alkyl substitution has been attempted as possible strategy [7–13]. The main advantage of this approach is the attainment of supramolecular ordering with consequent well-structured packing. This would extend the average conjugation length in regioregular polymers [14].

Among conducting polymers, polythiophenes occupy a prominent position because of their stability in the neutral

state [15–17] and their possible use in technologically advanced applications [18–33]. In this work the comparative study of electropolymerized poly 3',4' and 3,3''-didodecyl 2,2':5',2''terthiophenes (DDTTs) has been accomplished. The starting monomers are two isomeric regioregular systems with symmetric patterns of substitution (Fig. 1) [34]. The analysis of the results in terms of substituent position effects will then be presented.

2. Experimental

The starting monomers 3',4' and 3,3'' DDTT were prepared according to the procedure described in Ref. [35]. The electrochemical polymerization of 3',4' and 3,3''-DDTT was accomplished in the mixture acetonitrile(AN):benzonitrile(BN) with volume ratio = 4 : 1, with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. AN and BN were purchased from Aldrich. AN was dried by means of distillation over CaH_2 and P_2O_5 , BN was used as-received. TBAP was purchased from Fluka and was used without any further purification. Monomers concentrations ranged between 0.3 and 10 mM, TBAP

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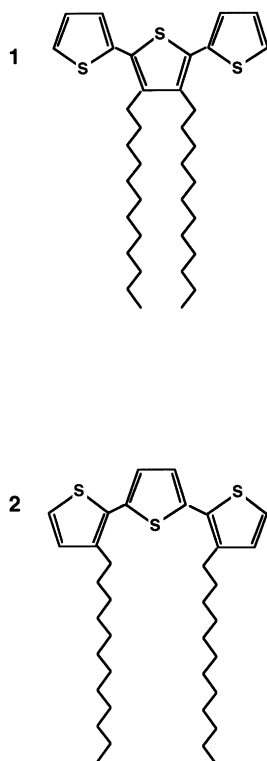


Fig. 1. Structures of the starting monomers (1) 3',4' and (2) 3,3''-didodecyl 2,2':5',2'' terthiophene (DDTT).

concentration was 0.1 M. Polymers were deposited potentiodynamically at the scan rates 20–100 mV s^{-1} onto Pt or Indium Tin Oxide (ITO) substrates in a three electrodes cell. ITO-covered glass was from Balzers and ITO-covered polyester from Bekaert. The counter electrode was a Pt wire, the reference electrode was Ag/AgNO₃ 0.01 M in acetonitrile [36]. All potential values in the text are referred to the latter ($E_{\text{Ag}/\text{AgNO}_3} = 0.34 \text{ V vs SCE}$). Polymerization processes were run in N₂ atmosphere. Ordinary electrochemical measurements were accomplished by means of a PAR potentiostat (EG & G, mod.362). The experimental set-up for fast electrochemical measurements (s.r. > 5000 V s^{-1}) has been described in Ref. [37]. The determination of the dimerization rate constant k_{dim} for DDTTs was accomplished by means of simulations of the fast scan rate cyclic voltammograms with B.A.S. DIGISIM 2.1 (Bioanalytical Systems, Inc., West Lafayette, IN 47906).

The geometries of the oxidized monomers were calculated with full optimization of the conformations using the semiempirical method UHF/AM1 [38]. The choice of this method was motivated by previous studies concerning substituted oligothiophenes [39]. In order to reduce the calculation time, the dodecyl groups were replaced by pentyl chains in the modelization. The charge densities were calculated from the optimized molecular geometries using the DFT theory with the B3LYP functional method [40] and the 6-31G* basis set [41]. Semiempirical calculations were made using the PC-Spartan software 1.1

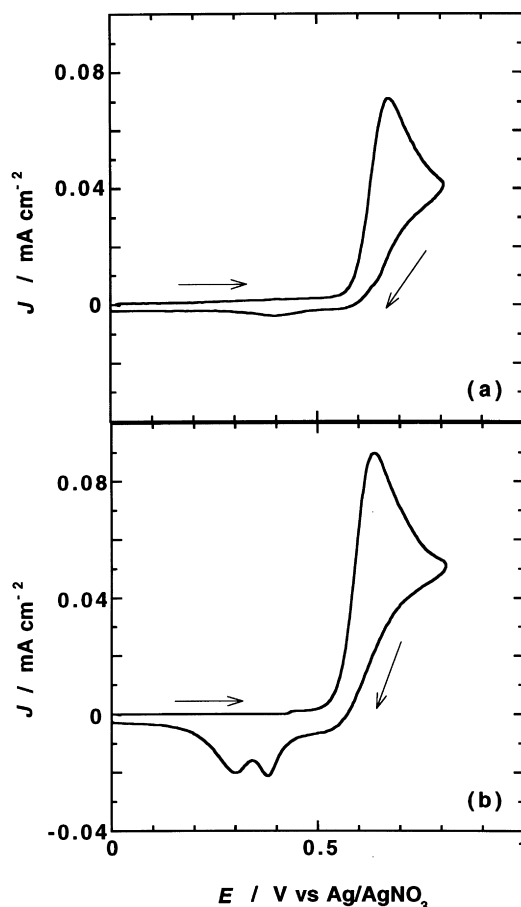


Fig. 2. First cyclic voltammetry of a solution containing: (a) 3',4'-DDTT 2 mM; and (b) 3,3''-DDTT 2 mM; TBAP: 0.1 M; AN/BN: 4/1 (volume ratio); scan rate: 100 mV s^{-1} .

(Wavefunction Inc., Irvine, CA) [42] and DFT calculations with the Gaussian 94w package [43].

IR reflectance spectra of DDTTs and poly-DDTTs in the neutral state were taken with a Perkin–Elmer System 2000 FT-IR. For the IR measurements, DDTTs were deposited onto ITO-covered glass dipping the ITO-substrate into the monomers at an immersion rate of $5 \times 10^{-2} \text{ cm s}^{-1}$. The monomers were sticky enough to produce a film with sufficient adhesion at the ITO-glass substrates. Poly-DDTTs were electrochemically deposited onto ITO-covered glass for the spectral measurements. The analysis of poly-DDTTs masses was made with the matrix assisted laser desorption ionization-mass spectrometry (MALDI-MS) [44,45] on the soluble fraction of poly-DDTTs in CHCl₃. In the MALDI-MS determinations the matrix was 2-para-hydroxyphenylazobenzoic acid (HABA). The calibration of the MALDI mass spectrometer was performed with angiotensin II and bovine insulin. Scanning Electron Microscopy (SEM) pictures were taken by means of a Cambridge 100 instrument with a resolution of 10 nm. Poly-DDTTs were electrochemically deposited on ITO-covered polyester for SEM pictures. The profilometer for thickness measurements was an Alpha-Step 200 from Tencor

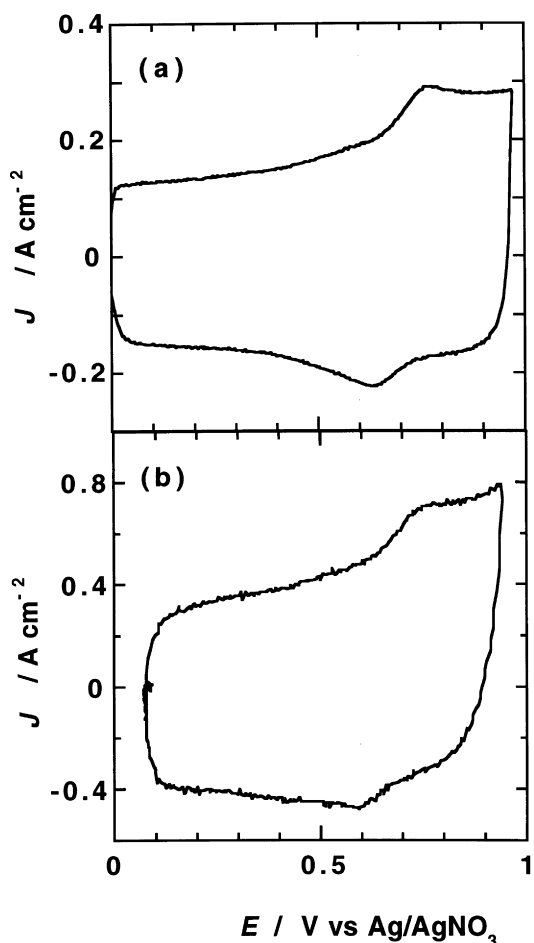


Fig. 3. Reversible cyclic voltammograms of: (a) 3',4'-DDTT; and (b) 3,3''-DDTT at 12 000 V s⁻¹; [3',4'-DDTT]: 3 mM and [3,3''-DDTT]: 10 mM; the diameter of Pt electrode was 10 μm.

Instruments. Poly-DDTTs were electrochemically deposited on ITO-covered glass for thickness measurements.

3. Results and discussion

The first cyclic voltammograms of 3',4'-DDTT and 3,3''-DDTT monomers are shown in Fig. 2. In the scan rate range 0.1–500 V s⁻¹, the oxidation peaks were irreversible for both monomers showing that radical-cations were highly reactive. In previous studies concerning the photochemical and electrochemical oxidations of substituted terthiophenes, it was demonstrated that dimer formation process involves the coupling of two radical-cations [42,46,47]. Therefore it is likely that the radical-cations of 3',4'-DDTT and 3,3''-DDTT follow a similar pathway for the production of new species which precipitate on the electrode. This can be seen from the shape of the reduction peak in the reverse scan (see Fig. 2). The comparison of the two voltammograms in Fig. 2 points out the existence of two distinct reduction peaks in the voltammogram of 3,3''-DDTT (Fig. 2b), whereas 3',4'-DDTT voltammogram (Fig. 2a), presents only one small

reduction peak during the reverse scan. Such difference should indicate that oxidized 3,3''-DDTT produces oligomers with relatively higher molecular weight with respect of oxidized 3',4'-DDTT in the timescale of the experiment [48]. The second cathodic peak of 3,3''-DDTT is centered approximately at 0.3 V (Fig. 2b, reverse scan), and it may be associated to the reduction of oligomeric species with longer conjugation length with respect of the species responsible for the cathodic peak at 0.4 V. The latter one is found in both voltammograms of Fig. 2, with different intensities and it can be ascribed to oligomeric species with the same number of 3',4'-DDTT and 3,3''-DDTT units. The potential values corresponding to the oxidation peak of the DDTTs are very close (0.62 and 0.64 V respectively for 3',4' and 3,3''-DDTT in Fig. 2). The oxidation potential of conjugated heterocyclic compounds can be properly evaluated when cyclic voltammograms of the species are run at very high scan rates (> 1000 V s⁻¹) [49,50]. In these conditions the reversible reduction of the radical cation can be detected before the occurrence of the chemical coupling process between radical cations. In Fig. 3 are shown the cyclic voltammograms of DDTTs at 12000 V s⁻¹. Formal potentials E° were immediately derived from these voltammograms as the half-sum between the forward and reverse scan peak potentials. We found $E^\circ = 0.73$ and 0.71 V vs Ag/AgNO₃, respectively, for 3',4'-DDTT and 3,3''-DDTT. The presence of alkyl substituents lowered the oxidation potential of the starting DDTTs ($E^\circ = 0.78$ V vs Ag/AgNO₃ for unsubstituted terthiophene)[42] as expected from the weak inductive effect associated with a donor group (C₁₂H₂₅). The strict similarity of E° values for DDTTs (0.73 and 0.71 V) is indicative of substantial equivalence in the electronic conjugation of the two isomeric monomers during the electron transfer process at the electrode. The effectiveness of the electronic conjugation in a molecule is related to its geometry. In the present case the calculation of the more stable conformations was accomplished for both oxidized monomers at the B3LYP/6-31G**/UHF/AM1 level [38]. We found that the more stable conformations of the oxidized monomers are quasi-planar with $\theta = 3.5$ and 1°, respectively, for the cation radicals 3',4'-DDTT^{·+} and 3,3''-DDTT^{·+}, where θ is the dihedral angle between terminal and central rings of the oxidized monomer. Such calculations showed that the monomer with the highest E° value, i.e. 3',4'-DDTT, possessed the more distorted configuration as determined by the highest value of θ . The simulation of fast scan rate voltammograms allows the evaluation of the dimerization rate constant k_{dim} assuming a coupling mechanism between radical-cations (see for example Ref. [42]). We derived $k_{\text{dim}} = 0.5 \times 10^7$ and 2.5×10^7 l mol⁻¹ s⁻¹, respectively, for 3',4'-DDTT^{·+} and 3,3''-DDTT^{·+}. Such results showed that DDTTs dimerization constants were lower than the value found for the dimerization of unsubstituted terthiophene ($k_{\text{dim}} = 2\text{--}3 \times 10^8$ l mol⁻¹ s⁻¹) [42]. The decrease of k_{dim} associated with the didodecyl substitution can be ascribed to the increase

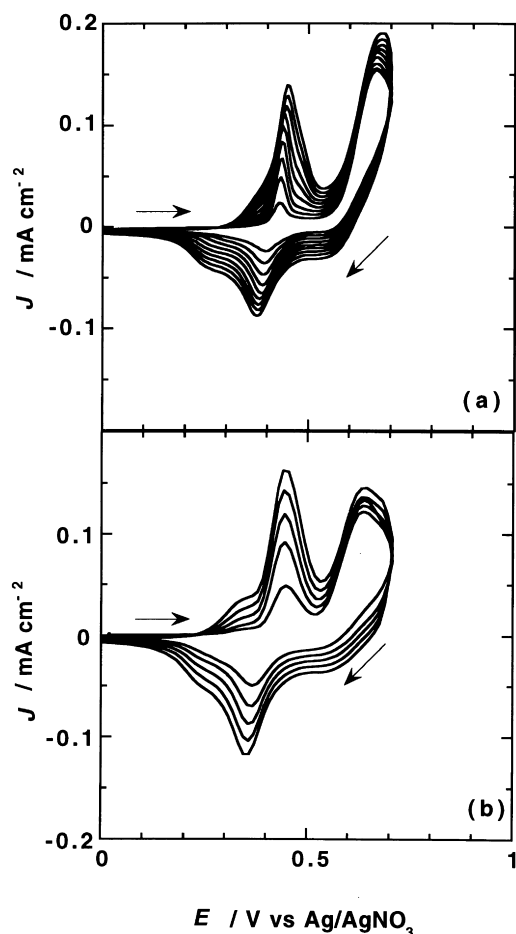


Fig. 4. Potentiodynamic electropolymerization of: (a) 3',4'-DDTT; and (b) 3,3''-DDTT; monomers concentration was 2 mM; TBAP: 0.1 M; AN/BN: 4/1 (volume ratio); scan rate: 100 mV s⁻¹. Data are shown from the fourth cycle on.

of the molecular mass (>100%) induced by the introduction of alkyl groups in the terthiophene skeleton. Such mass augmentation depresses the mobility and the solubility of the starting monomers in the synthesis solution decreasing the reactivity in the coupling reaction. The comparison of k_{dim} values for DDTTs accounts for the difference between the isomers reactivities in the oxidative coupling reaction [51]. The weak inductive effect associated to the dodecylic group should promote the localization of the unpaired electron on the substituted ring of the radical cation [5]. Calculations of the spin density distribution in the oxidized monomers with the reported geometries, show that the central ring of the 3',4'-DDTT^{•+} has a fractional spin density equal to 0.35 whereas terminal rings have the value 0.27. The difference of the fractional spin density between central and terminal rings of 3,3''-DDTT^{•+} cation radical is relatively lower (calculated fractional spin densities are 0.28 and 0.31, respectively, for central and terminal rings) because of the diminution of the donor groups number in the substituted ring. The radical cation of the monomer 3,3''-DDTT is expected to couple faster

than the radical cation of 3',4'-DDTT for the higher ratio of spin density on the external rings.

The proportion of unpaired electron on the terminal rings represents one of the major contributions to the reactivity of the radical cation in the oxidative dimerization. Other factors such as steric hindrance, electrostatic repulsion, stability of the produced dimer, geometry and energy of the transition states should be also considered for the evaluation of monomers reactivities.

The potentiodynamic electropolymerization of DDTTs at 100 mV s⁻¹ is shown in Fig. 4. The upper potential limit for DDTTs polymerization was 0.7 V vs Ag/AgNO₃. Such value is just above the oxidation peak of the monomers (see Fig. 2). This precaution was taken in order to avoid oxidative irreversible degradation of the resulting polymer [52]. The cycling brings about the appearance of a new reversible oxidation peak centered at about 0.46 and 0.40 V vs Ag/AgNO₃, respectively, for 3',4'-DDTT and 3,3''-DDTT. This second peak is associated to the formation of light oligomeric species (namely dimers or trimers), as deducible from the corresponding potential values [53]. The shoulders surrounding these peaks can be ascribed to the presence of polymeric species with a polymerization degree higher than 5–6 monomeric units [54]. The peak current intensity increases with the number of cycles. Moreover, the separation between the potential values of the oxidation and reduction peaks enlarges with the number of cycles. These findings indicate the thickening of the polymeric film and the diffusion control in the rate of the electrochemical doping/undoping processes [55]. The most relevant difference between electropolymerization of 3',4'-DDTT and 3,3''-DDTT is associated with the rate of increase of the current intensity per cycle. In fact during the polymerization of 3,3''-DDTT (Fig. 4b), the oxidation peak at lower potential reaches the value 0.15 mA cm⁻² just after eight cycles (first three cycles are not displayed in Fig. 4 for both electropolymerizations), whereas the corresponding peak of 3',4'-DDTT (Fig. 4a) takes 12 cycles to reach the same current value. Such behaviors are associated to the diverse kinetics of precipitation for the species obtained from the combination of the isomer monomers. The differences could be ascribed to the higher reactivity of the radical cation resulting from the oxidation of 3,3''-DDTT, which couple faster than the other isomer cation. Consequently, the polymerization degree will result differently for the two isomers in the same experimental conditions. Moreover it has been verified that the species produced by the coupling of 3,3''-DDTT precipitate faster than those obtained by 3',4'-DDTT. The latter has been ascribed to the different solubilizing properties of the alkylic chains due to their positions [56]. Polymer thickness measurements with a profilometer showed that the deposition yield for poly 3',4'-DDTT varied between 8 and 18 nm per 1 mC cm⁻² of charge density when the amount of deposited charge ranged between 400 and 700 mC cm⁻². This means that poly 3',4'-DDTT film density changed with the progress

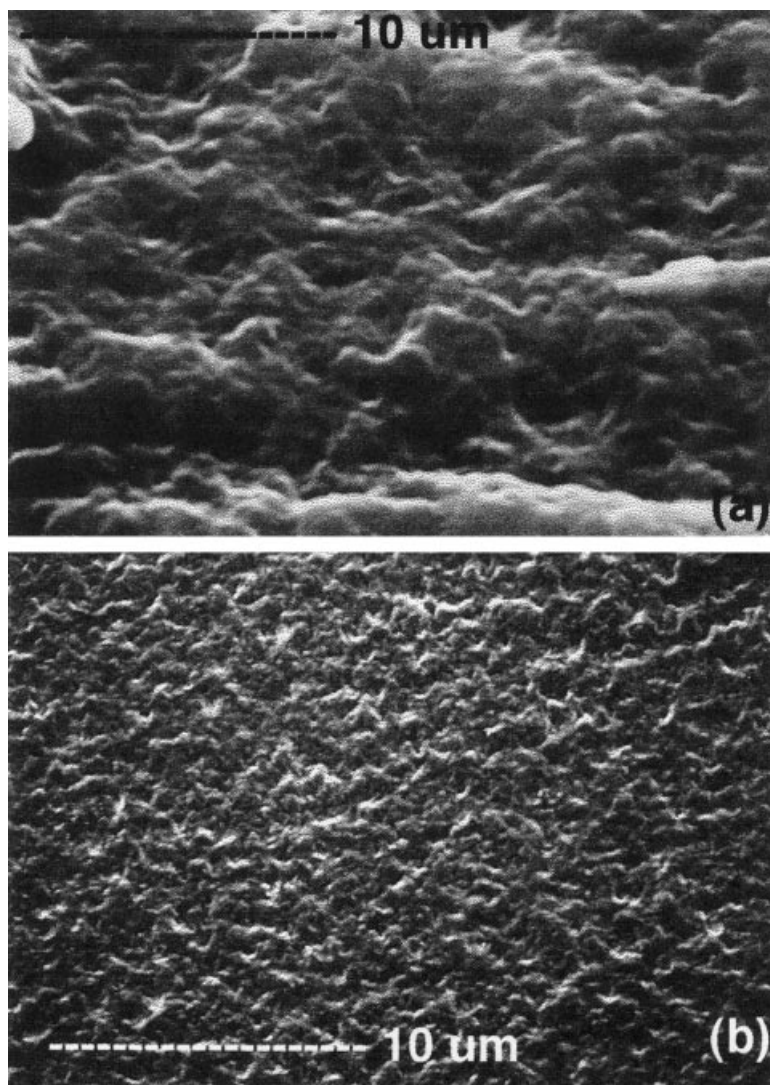


Fig. 5. SEM pictures of: (a) poly 3',4'-DDTT; and (b) poly 3,3''-DDTT deposited onto ITO-covered polyester. Deposition charge was 90 mC cm^{-2} for both poly DDTTs (deposition scan rate: 20 mV s^{-1}).

of polymerization as found in other polythiophenes [57–59]. Thinner films of 3',4'-DDTT could not be characterized with the profilometer because they were mechanically unstable. Analogous measurements of poly 3,3''-DDTT thickness could not be accomplished for the scarce adhesion of poly 3,3''-DDTT to the ITO substrate when charge exceeded 150 mC cm^{-2} . This was due to the inclusion of large amounts of solvent in the electrodeposited film.

The SEM pictures of neutral electrodeposited poly DDTTs are shown in Fig. 5. The morphologies of the two isomer polymers were quite different despite of the same amount of deposited charge (90 mC cm^{-2}) estimated from the time-integration of the current in the cyclic voltammograms. In fact poly 3',4'-DDTT (Fig. 5a) presented a smoother surface with respect of poly 3,3''-DDTT (Fig. 5b). The different morphologies could be ascribed to the different amounts of solvent included because of the diverse poly DDTTs solubilities in the synthesis electrolyte.

In fact it has been verified that the starting monomer 3,3''-DDTT is more soluble than the isomer 3',4'-DDTT in the electrolyte used for the electrochemical polymerization [the solubilities of 3',4'-DDTT and 3,3''-DDTT were, respectively, 6 and 15 mM at room temperature in AN : BN = 4 : 1 (volumeratio)].

The MALDI-TOF mass spectra of the soluble fractions of poly-DDTTs in CHCl_3 are listed in Table 1. The maximum degrees of polymerization are 11 and 7, respectively, for 3',4'-DDTT and 3,3''-DDTT (Table 1). This result is seemingly in contradiction with the cyclic voltammetry evolution of isomer 3,3''-DDTT (Fig. 4) which showed the existence of longer chains for the polymerization products of 3,3''-DDTT. This discrepancy is only apparent because the mass spectra do not refer to the poly DDTTs fractions insoluble in CHCl_3 . The cyclic voltammeteries of the poly DDTTs fractions insoluble in CHCl_3 (Fig. 6), show for poly 3,3''-DDTT a lower value for the potential corresponding to

Table 1

Listed MALDI-TOF mass spectra of soluble poly 3',4'-DDTT and poly 3,3''-DDTT fractions in CHCl₃. The matrix-compound was 2-parahydroxyphenylazobenzoic acid (HABA)

Peaks position/a.m.u. (intensity/a.u.) ^a		Assignment/theoretical mass values
3',4'-DDTT	3,3''-DDTT	
		587
1173 (7400)	1173 (7500)	(DDTT) ₂ /1172
1206 (1400)	–	(DDTT) ₂ + O ₂ /1204
1757 (1800)	1758 (800)	(DDTT) ₃ /1757
2342 (1500)	2343 (1400)	(DDTT) ₄ /2342
2927 (600)	2929 (400)	(DDTT) ₅ /2927
3511 (400)	3514 (400)	(DDTT) ₆ /3512
4098 (220)	4099 (300)	(DDTT) ₇ /4097
4682 (180)	–	(DDTT) ₈ /4682
5262 (160)	–	(DDTT) ₉ /5267
5855 (120)	–	(DDTT) ₁₀ /5852
6432 (140)	–	(DDTT) ₁₁ /6437

^a Note that peak position is systematically shifted by +1 a.m.u. because of the protonation of the sampled molecule in MALDI-TOF experiments.

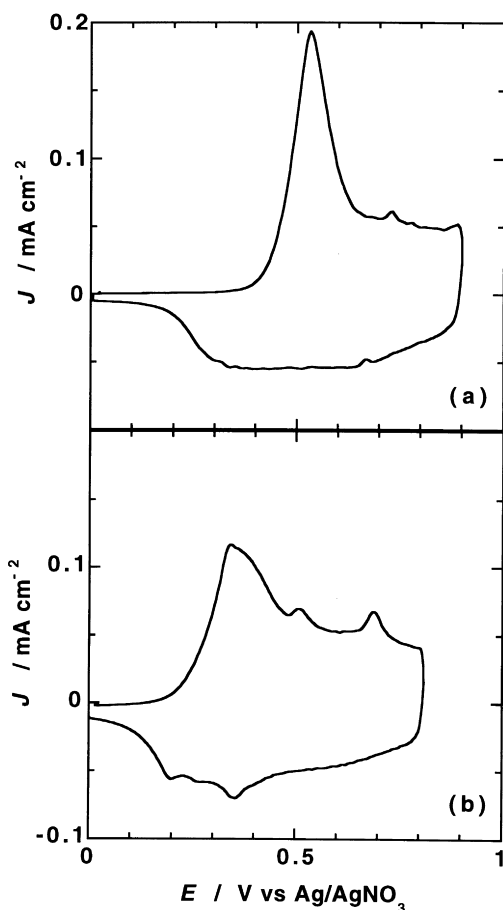


Fig. 6. Cyclic voltammeteries in monomer-free solutions of: (a) poly 3',4'-DDTT; and (b) poly 3,3''-DDTT fractions insoluble in CHCl₃; the solution was AN/BN = 4/1 with TBAP 0.1 M (scan rate: 100 mV s⁻¹).

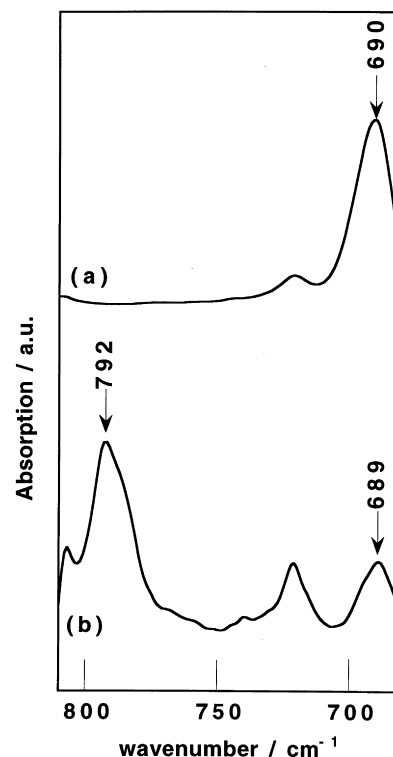


Fig. 7. IR spectra of: (a) 3',4'-DDTT; and (b) poly 3',4'-DDTT onto ITO in the wavenumbers range 680–810 cm⁻¹; poly 3',4'-DDTT deposition charge was 20 mC cm⁻².

the anodic current peak. This would confirm the higher degree of polymerization for poly 3,3''-DDTT. Unfortunately, the MALDI-TOF mass spectrum can not be used for a quantitative evaluation of the mass distribution. This because the peak intensity does not depend solely on the actual number of analyzed molecules but also on the effectiveness of the coupling between the matrix (HABA) and the species analyzed during the desorption process [45].

In the case of polythiophenes the IR spectra can give valuable informations on the polymerization degree, the effectiveness of electronic conjugation and the positions of the monomer involved in the coupling process [54,60]. In Figs. 7 and 8 the comparison of poly DDTTs IR spectra with those of parents monomers are shown in the range 680–810 cm⁻¹. The examined region refers to the vibrations out of plane of the C–H bonds in the thiophene ring [61–63]. The band approximately centered at 690 cm⁻¹ is associated to the bending of the C_β–H bond in a thiophene substituted in the position 2, whereas the band at about 790 cm⁻¹ is ascribed to the bending of the C_β–H bond in a disubstituted thiophene in the positions 2 and 5 [61,62]. Therefore the monomer 3',4'-DDTT will show in the examined range (Fig. 7a) the sole band at 690 cm⁻¹ due to the absence of H atoms in the β position of the middle ring (Fig. 1a). The electrochemical polymerization of 3',4'-DDTT brings about the lowering of the intensity for the band at 690 cm⁻¹ and the appearance of a new band at 792 cm⁻¹ in

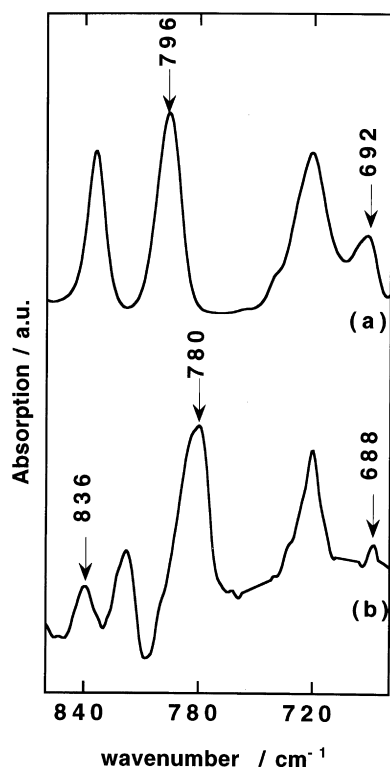


Fig. 8. IR spectra of: (a) 3,3''-DDTT; and (b) poly 3,3''-DDTT onto ITO in the wavenumbers range 680–860 cm^{-1} ; poly 3,3''-DDTT deposition charge was 20 mC cm^{-2} .

the IR spectrum (Fig. 7b). The latter band is due to the formation of new thiophenes units in the polymeric chain possessing simultaneously $\text{C}_\beta\text{-H}$ bonds and a substitution pattern involving 2 and 5 positions. Therefore, it is reasonable to deduce from the modifications of the IR spectra the elimination of the H atoms in α (position during the oxidative coupling process). On the contrary the polymerization of 3,3''-DDTT induces a change in the relative intensity of the band located between 770 and 800 cm^{-1} with respect of that approximately centered at 690 cm^{-1} (Fig. 8). Such spectral change corresponds to the augmentation of the relative intensity of the band at higher wavelength numbers in Fig. 8b. Poly 3,3''-DDTT should present qualitative differences in the nature of $\text{C}_\beta\text{-H}$ bonds with respect of the parent monomer if the oxidative coupling of 3,3''-DDTT involves the $\alpha\text{-H}$ elimination. After 3,3''-DDTT polymerization a new band centered approximately at 836 cm^{-1} appears (Fig. 8b). This band can be associated to the presence of $\text{C}_\beta\text{-H}$ bonds belonging to a 2,3,5 substituted thiophene ring [63]. In this case a 2,3,5 substituted thiophene ring can be originated if the coupling process of 3,3''-DDTT (Fig. 1b) involves the elimination of $\alpha\text{-H}$ atoms. This is indicative of the fact that the electropolymerization of 3,3''-DDTT mostly produces a polymeric system with an effective electronic conjugation [14].

The analysis of the structures of the species present in the soluble fraction of poly-DDTTs in CHCl_3 was also

accomplished with ^1H NMR. The resulting spectra (not shown here) presented the typical features of the stereoregular polymers with $\alpha\text{-}\alpha$ linking as verified by the resonances in the aromatic and aryl-methylene regions [35].

4. Conclusions

The pattern of substitution in regioregular didodecylterthiophenes, e.g. 3',4' and 3,3''-2,2':5',2'' didodecylterthiophene, had a relevant influence on the properties of the resulting electrodeposited polymers. The rate of film formation was highest in the case of 3,3''-2,2':5',2'' didodecylterthiophene electropolymerization. This was mainly ascribed to the different reactivities of the radical cations produced by monomers oxidation. Electrodeposited polymeric films were formed by chains with different lengths as detected with mass spectrometry. Systems with the higher polymerization degree were produced in 3,3''-didodecylterthiophene electropolymerization.

SEM pictures revealed substantial differences in the morphologies of the isomeric polymers grown in the same experimental conditions. In the case of poly 3',4'-didodecylterthiophene, the profilometric technique showed the non-homogeneous growth of the electrodeposited polymer film. IR and ^1H NMR spectra of both poly-didodecylterthiophenes indicated a predominant $\alpha\text{-}\alpha$ coupling during electropolymerization. The comparison of the oxidation potential values for the isomeric monomers showed that substitution pattern had no relevant influence in the electron transfer process at the electrode.

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