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***In-situ* measurement of the conductance of regioregular poly-3',4'-didodecyl-2,2':5',2''-terthiophene during potentiodynamic growth**

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Abstract

This work reports a study of regioregular poly-3',4'-didodecyl-2,2':5',2''-terthiophene (poly-3'4'-DDTT) deposited electrochemically onto a double-band electrode for the *in situ* measurement of the electrical conductance. The electrodeposition of poly-3'4'-DDTT was conducted in the potentiodynamic mode within the applied potential interval $0 \leq E_{\text{appl}} \leq 0.9 \text{ V vs Ag/Ag}^+$ employing an electrolyte that contained the terthiophenic monomer 3'4'-DDTT (the starting redox species). These electrochemical conditions warrant the oxidation of 3'4'-DDTT (initiation step) and prevent the oxidative degradation of the polymerization product(s). Through the adoption of conformal mapping we could calculate the electrical conductivity, σ , of the electrodeposited polymer thanks to the observation of a linear variation of conductance with the consumed charge of polymerization. Moreover, the use of conformal mapping for the analysis of these phenomena of electrochemical growth of a conducting deposit has allowed also the determination of the volume yield for the poly-3'4'-DDTT under consideration. The electrical conductivity of poly-3'4'-DDTT depended nonlinearly on the scan rate of electrodeposition and varied in the broad range $12 < \sigma < 34 \text{ S cm}^{-1}$. This has allowed the identification of the optimal conditions of electrodeposition for achieving highly conductive poly-3'4'-DDTT at ambient temperature. The variability of poly-3'4'-DDTT conductivity depended on the nature of the electrodeposit which, in turn, depended on the rate of oxidative coupling (determined by the electrical current) and on the rate of precipitation (determined by the conditions of saturation in proximity of the double-band electrode).

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Introduction

Polythiophenes (PTs) [1] are conjugated polymers with high chemical stability[2] which can be successfully employed in many relevant applications[3,4] like solar energy conversion,[5-8] energy storage, [9,10] organic electronics [11,12] and electrochromism.[13-15] Such a versatility in PTs stems from their capability of switching rapidly and reversibly their electrical conductivity through the application of very diverse types of stimuli, e.g. electrochemical, electrical, optical, magnetic, thermal, chemical or biological.[16-29] Another strength of PTs is the possibility of obtaining them in diverse physical states[30,31] and configurations/morphologies[32-34] through a great variety of well-established synthetic procedures.[35-40] In addition to that, the combination of such favourable aspects in PTs can also lead to the realization of new-generation devices in which PTs, in the role of active materials, are designed and configured for possessing dynamic features[41-44] and accomplishing smart functions.[45-48] Electronically conducting polymers like PTs can be synthesized through two main routes: via chemical or electrochemical polymerization.[49] Both routes involve an analogous mechanism of polymerization, i.e. the oxidative coupling of the monomer, in which is important to control the initiation, propagation and termination of the chain in order to achieve a conjugated polymer with defined chemical composition, extent of conjugation, chain length, physical state and morphology.[50] The adoption of the electrochemical approach for the synthesis of PTs has to be preferred for various reasons[51]:

- a) It does not need of a catalytic agent that has to be removed at the completion of polymerization. Consequently, the electropolymerized systems result more pure than the analogous chemical counterpart and do not need further processes of purification/separation from the medium of polymerization given the heterogeneous nature of the process of electrodeposition which requires exclusively the extraction of a polymer-coated electrode
- b) The duration of electropolymerization is directly controllable by the electrochemical experimental set-up thus allowing the modulation of the thickness of the polymeric deposit within a wide range of values (from few Angstroms to several microns)
- c) The possibility of varying substrate material, the chemical nature of the constituents of the electrolyte and the electrochemical parameters (i.e. current intensity, potential value or scan rate if the electropolymerization is conducted respectively in the galvanostatic, potentiostatic or potentiodynamic mode) affords the attainment of conjugated polymers that can display very different chemical, morphological, structural and physical properties

With regard to the preparation of PTs via the electrochemical route,[52-54] the synthesis of these conjugated polymers through the electrochemical oxidation of terthiophenes (TTs) as starting monomers (either symmetrically[41,55-57] or asymmetrically[58-60] substituted) has been recognized as particularly advantageous[61,62] with respect to the electrodeposition of PTs from single thiophene ring [63] or dimeric precursors (bithiophenes).[64-70] This because the electrodeposition of PTs from TT-based monomers generally requires the application of lower oxidation potential values for triggering the mechanism of oxidative coupling with respect to shorter starting monomers.[71,72] The use of TT monomers would then avoid the problem of oxidative degradation (overoxidation) that is typical of PT electrochemical synthesis from single-rings or dimers.[73,74] For this reason we have considered in the present work the study of the conductivity properties of electrochemically deposited, regioregular poly-3',4'-didodecyl-2,2':5',2''-terthiophene[41,56,70] (poly-3'4'-DDTT, right sketch in Figure 1) employing an *in situ* conductimetric method[75,76] when the starting monomer is 3'4'-DDTT (left sketch in Figure 1). The adopted conductimetric method allows the determination of the electrical conductance in a polymer during its potentiodynamic growth when the polymer is deposited in the configuration of thin film (i.e. with thicknesses lower than 10 μm) onto a double-band electrode (Schemes 1 and 2). The availability of *in situ* characterization methods is generally advantageous for the study of switchable materials like PTs, especially for the observation of the evolution of the redox/physical properties.[77-79] In addition to that, *in situ* characterization methods can be also exploited for the analysis of the mechanism of PT electrochemical growth.[41,56,80,81] Among various types of information *in situ* characterization methods can provide on conjugated PTs,[82] the most useful one is the electrical conductivity [83] since the latter property is recognized as fundamental and distinctive for this class of organic materials.[84] This becomes more evident if we consider that the switching of any chemical-physical property of PTs is systematically accompanied by an alteration of their electrical conductivity.[27,28,85,86] Since poly-3'4'-DDTT is grown electrochemically via oxidative coupling of the terthiophenic monomer 3'4'-DDTT (Figure 1, left sketch),[51-54,87] the results presented here will refer to the *p*-type conductivity [88] of poly-3'4'-DDTT. To our knowledge this work is one of the first reporting the *in situ* determination of electrical conductivity in a regioregular system like poly-3'4'-DDTT during its potentiodynamic growth. The PTs obtained from regioregular starting monomers,[57,59,89] like in the present case, attract interest because the resulting polymers can display peculiar properties related to solid state chirality [90,91] in addition to the well-acknowledged switching properties that are typical of any PTs (*vide supra*).[16-29,92,93] Moreover, regioregular PTs[94,95] like poly-3'4'-DDTT are

thoroughly investigated nowadays for their employment as hole-transporting layers (HTLs) in perovskite solar cells.[96-103] At the basis of this interest in regioregular substituted PTs there is the motivation of designing and producing efficacious HTL materials [104-106] that replace expensive spiro-OMeTAD.[107-109] The presence of an ordered pattern of large hydrophobic substituents, i.e. the dodecyl pending groups in poly-3'4'-DDTT (Figure 1, right sketch), can motivate reasonably the eventual employment of poly-3'4'-DDTT as HTL in perovskite solar cells. This because humidity is recognized as a problematic presence in this type of solar conversion devices. Therefore, hydrophobic dodecyl groups can exert a protective action in addition to the function of hole transport.[110] On the basis of these considerations the *in situ* determination of the *p*-type conductivity in regioregular PTs like the poly-3'4'-DDTT here considered (Figure 1, right sketch) can result then useful also in the ambit of perovskite photovoltaics.[111]

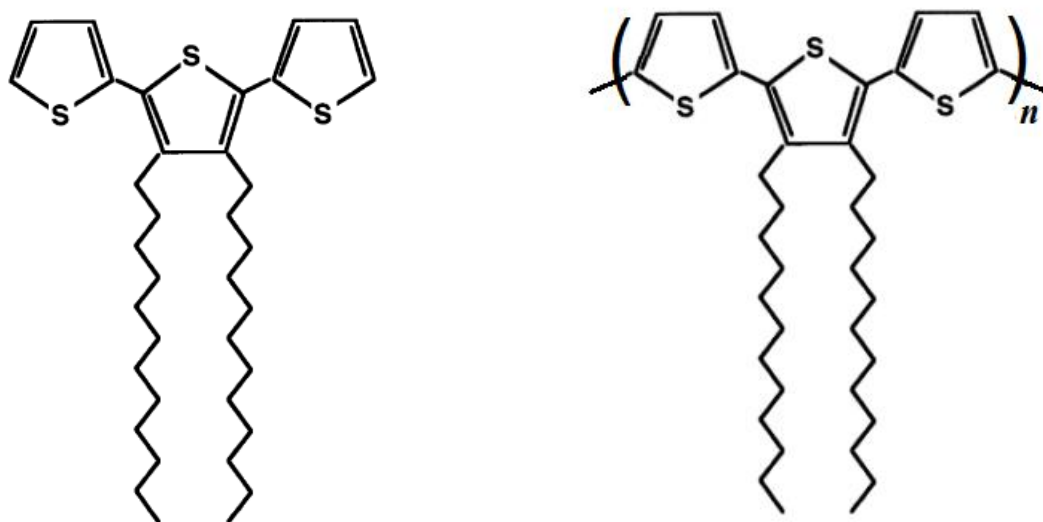


Figure 1: Structure of the monomer 3'4'-DDTT (left) employed as precursor for the electrochemical deposition of poly-3'4'-DDTT (structure on the right).

Experimental section

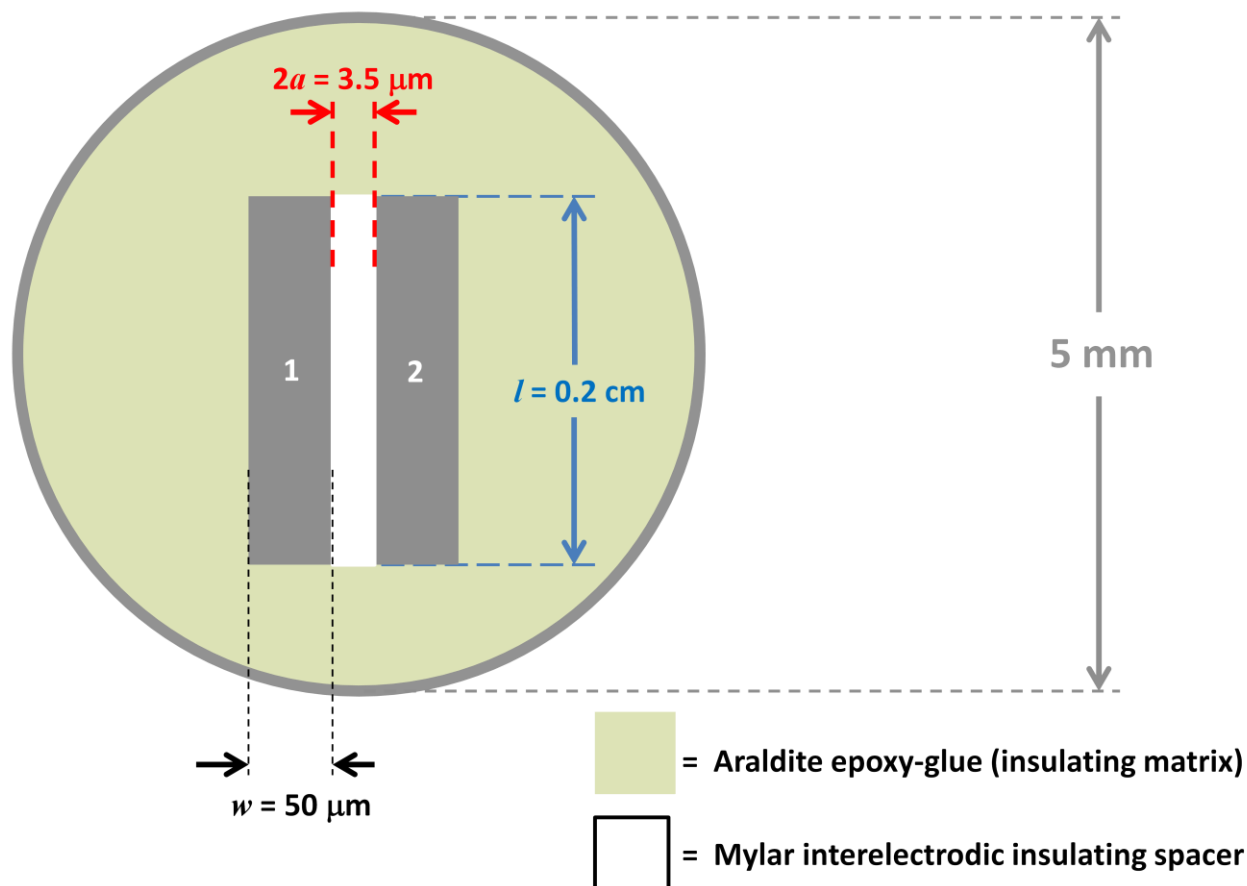
Reagents and polymer preparation. Regioregular terthiophene 3'4'-DDTT (Figure 1, left sketch) represents the starting material of this work. It has been prepared according to the synthetic procedure developed by Andreani and its group.[112] The procedure is based on Grignard coupling of heterocyclic compounds for the selective alkylation of the thiophene rings in β -positions [113].

The purity of 3'4'-DDTT was higher than 90% and it was ready to be used as monomer for the deposition of the corresponding polymer via electrochemical oxidative coupling. The details of the procedure of the electrochemical deposition of poly-3'4'-DDTT (Figure 1, right sketch) have been previously reported in several papers by our group.[45,77,114,115]

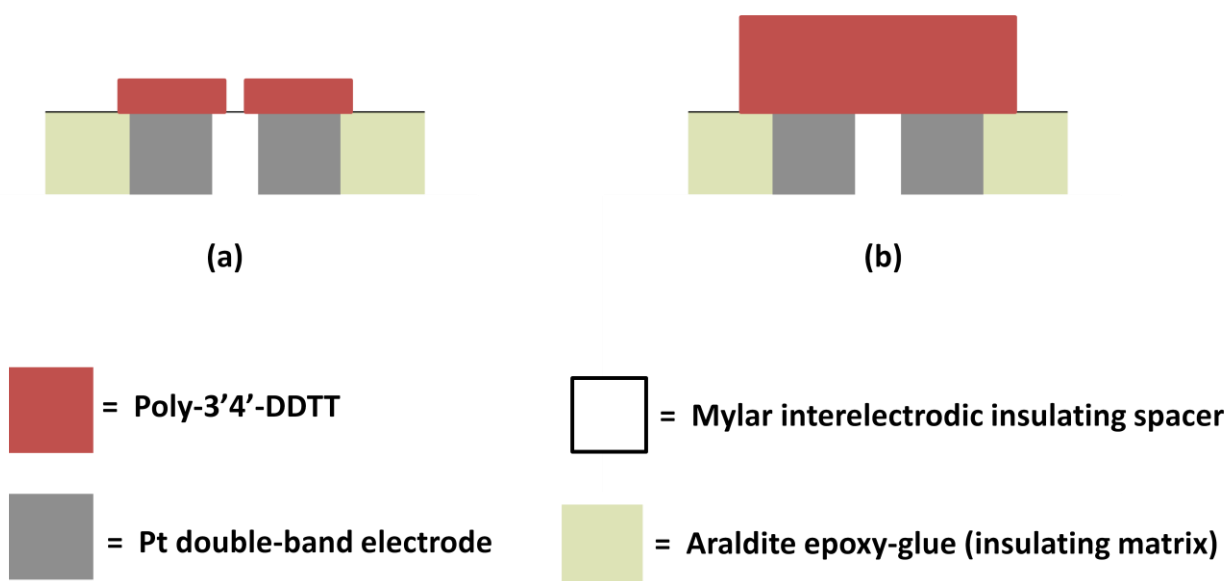
In situ conductimetry. The experimental set-up for the realization of *in-situ* conductimetry on poly-3'4'-DDTT makes use of a double-band electrode as working electrode, which represents the substrate onto which the electroactive polymer is potentiodynamically grown.[45,75,76] As reported in ref. 116, the double-band electrode consists in a pair of two conducting foils of Pt with the same width and thickness, which are separated by an insulating plastic layer of Mylar. The three layers are held together compactly within an electrically insulating matrix of epoxy-resin glue (Scheme 1). Given the plastic nature of the insulating separator, the thickness of the Mylar layer can deviate from its nominal value. For this reason the thickness of the interelectrode separator needs to be evaluated photographically each time after the assemblage of the double-band electrode since its actual value affects the calculation of the conductance of the bridging electroactive polymer (*vide infra*).[75,116] The polished section of the double-band electrode (Scheme 1) represents the part in direct contact with the electrolyte containing the starting monomer. Poly-3'4'-DDTT is potentiodynamically grown [41,70,81] onto the two contiguous slides constituting the double-band electrode via oxidative coupling of the monomer.[54] The electrochemical growth of poly-3'4'-DDTT proceeds separately on the two bands till the two (hypothetically symmetric) deposits overlap and create a polymeric bridge connecting electrically the two bands (Scheme 2). Polymer bridge formation occurs thanks to the lateral growth of the electrodeposits. Because of the latter phenomenon, the width of the interelectrode spacer should be relatively small with respect to the electrode width in order to apply conformal mapping.[117,118] The lateral growth of the polymer externally to the double band electrode (i.e. on Araldite considering the sketch of Scheme 1) should be minimal in order to minimize the errors done in the geometrical transformation of a system made of two adjacent slabs that lie onto side-by-side bands into a single layer sandwiched between two facing bands in accordance to conformal mapping.[75] In fact, it is through the use of conformal maps that is possible to map a double-band electrode into a closed box [75] and determine then the conductivity properties of a thin deposit provided that the polymeric slab obeys Ohm's law. Actually, the polymer grows only on one conductive substrate and not between two parallel electrodes facing each other, [75,79] and it is through conformal mapping that the actual polymeric electrodeposit can be rendered equivalent to a sandwiched slab.

For the *in situ* measurement of poly-3'4'-DDTT conductance a small potential difference of 1 mV was applied between the two bands, the potential stimulus being imparted as a sinusoidal wave at the frequency 130 Hz. The a.c. response was measured on a lock-in amplifier (model SR 830, Stanford Research Instruments).

1 and 2 are two nominally equivalent electrodic bands of Pt. The drawing is a not to scale representation of the exposed end of a double-band working electrode



Scheme 1. Schematic depiction of the double-band electrode used in the present work. The rectangles 1 and 2 stand for two nominally equivalent electrodic bands of Pt. The relative sizes of the various electrodic parts are not to scale. The section here depicted represents the bottom of the double-band electrode which is exposed to the electrolyte. Both Araldite and Mylar are insulating materials that provide electrical insulation between the two electrodic bands. Symbols w , a and l refer to the electrode-band width, to the half-width of the interelectrode spacing and electrode-band length, respectively.



Scheme 2. Section of a double-band electrode and growth profile for a polymeric electrodeposit onto this. In the conduction of this experiment two main stages of growth are distinguished: (a) prior the formation of the lateral bridge (early stadium of the growth); (b) after the formation of the polymeric bridge that connects electrically the two bands (terminal stadium of the growth).

Results and discussion

The electrochemical growth of poly-3'4'-DDTT has been conducted potentiodynamically onto the two-bands electrode at three different scan rates (10^{-3} , 10^{-2} and 10^{-1} V s⁻¹) with the applied potential varying in the same range $0 \leq E_{\text{appl}} \leq 0.9$ V vs Ag/Ag⁺ (single anodic scan). The current profiles reproduce very well the results presented previously in refs. [41](#) and [115](#).

The corresponding evolutions of the electrical conductance (G) of poly-3'4'-DDTT with the consumed charge density (Q) are shown in Figure 2.

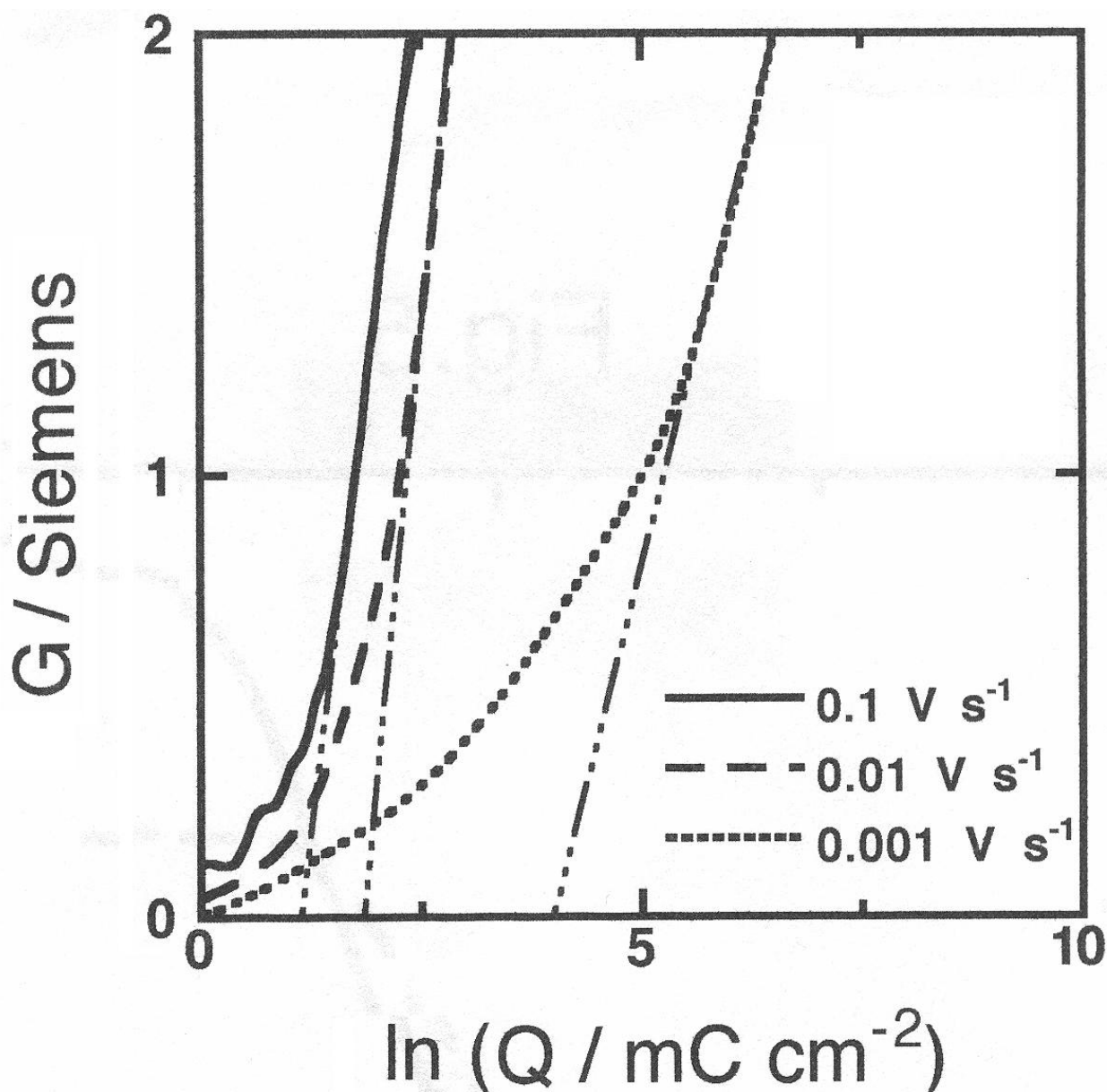


Figure 2. *In situ* variation of the conductance of a poly-3'4'-DDTT film with the logarithm of the anodic charge during potentiodynamic oxidative electropolymerization. The conductance profiles have been recorded at the three different scan rates indicated in the right bottom corner. In the figure the dotted lines evidence the slope of the linear portions of the three conductance profiles. The values of the intersections of the linear fits with the X-axis are used for the determination of polymer conductivity (see text).

In accordance to the model developed in ref. [75], we consider in the X-axis the consumed charge density Q as independent variable. For the evaluation of the latter parameter we have considered the area $w \cdot l$ of a single electroodic band (sides: $50 \mu\text{m} \times 0.2 \text{ cm}$, Scheme 1) consistently with the approach of conformal mapping of the polymeric deposit.[75] Since the polymer is grown potentiostatically, i.e. at a non even rate (different to the case of a galvanostatic growth),[75] the equation of the conductance (G) will have the general form:

$$G = \frac{\sigma l}{\pi} \left[\ln \left(\frac{8\eta Q}{\pi a} \right) \right] \quad \{1\}$$

assuming that the conducting polymer holds an ohmic behaviour (with constant conductivity) in the linear regime of the curve G vs $\ln(Q)$ curve, and that the consumed charge is spent exclusively for expanding a system which is already in its highest conductive state.[45,114] In Eq.1 the parameters σ , l , η , Q and a represent the polymer conductivity (in S cm⁻¹), the length of the electrodic bands (= 0.2 cm from the sketch in Scheme 1), the volume yield of the polymer (in m³ C⁻¹), the consumed charge density (in C m⁻²) and the half-width of the interelectrode spacer (in m), respectively. The width of the polymer bridge is equal to the interelectrode spacing and has the value 3.5 μm (= 2a) in the present work. In the adopted experimental conditions of potentiostatic growth, the current density j (= $\frac{dQ}{dt}$, by definition) is not constant and varies with the applied potential and with time (t), i.e. $j = f(t)$. This implies that in the potentiostatic mode of polymer growth the drawing of the three conductance plots of Figure 2 requires the time-integration of the recorded current density in order to compile the column of Q data to show on the X-axis. Since $Q = \int_0^t j(t)dt$, Eq.1 can be rewritten in the equivalent form

$$G = \frac{\sigma l}{\pi} \left[\ln \left(\int_0^t j(t)dt \right) + \ln \left(\frac{8\eta}{\pi a} \right) \right] \quad \{2\}$$

to indicate explicitly the time-dependence of the current density and of the consumed charge density (the latter represents the independent variable of Figure 2). The graphical determination of the slope and the intercept of Eq.2 allows the calculation of polymer conductivity and volume yield, respectively, provided that electrode length and interelectrode spacing are known (Eq. 2). Table 1 presents the parameters obtained from the analysis of the linear portions of the three conductance curves of Figure 2.

Scan rate / V s ⁻¹	$\Delta G/\Delta \ln Q' / S$	$[\ln Q']_{G=0 s}$	$\sigma / S \text{ cm}^{-1}$	$\eta / \text{cm}^3 \text{ C}^{-1}$
0.001	0.82	3.937	12.9	$1.34 \cdot 10^{-3}$
0.01	2.13	1.812	33.4	$1.12 \cdot 10^{-2}$
0.1	1.60	1.125	25.1	$2.23 \cdot 10^{-2}$

Table 1. Values of poly-3'4'-DDTT parameters σ (conductivity in the second column from right) and η (volume yield in the first column from right) as determined via Eq.2 after the analysis of the linear portions of the conductance curves of Figure 2. With regard to the linear portions of the three curves recorded at different scan rates, the second and third column from left report the corresponding slopes and the intercepts on X-axis, respectively. The symbol Q' indicates the ratio $Q/mC \text{ cm}^{-2}$, i.e. the charge density normalized with respect to the chosen unit.

The value of the linear slope $\frac{\Delta G}{\Delta \ln(Q')}$ (second column from left in Table 1) corresponds to the

ratio $\frac{\sigma l}{\pi}$ whereas the X-axis intercept of the prolongation of the linear portion, i.e. $[\ln Q']_{G=0 s}$

(third column from left in Table 1), corresponds to the logarithm $\ln\left(\frac{\pi a}{8\eta}\right)$. The determination of

X-axis intercept leads to the evaluation of the volume yield per unit charge through the relationship

$$\eta = \frac{\pi a}{8Q'} \quad \{3\}$$

Both *in situ* conductivity and volume yield of poly-3'4'-DDTT depended on scan rate (Table 1). In particular, conductivity varied non linearly with the scan rate since σ oscillated from a minimum of 12.9 S cm^{-1} (achieved at the slowest rate of 0.001 V s^{-1}) to a maximum of 33.4 S cm^{-1} (achieved at the intermediate scan rate of 0.01 V s^{-1}). When the conductivity of poly-3'4'-DDTT is determined *ex situ* through a potentiostatic experiment the maximum value achievable of conductivity is $\sigma_{\text{MAX}} = 33 \text{ S cm}^{-1}$. [45] The coincidence of the *ex situ* and *in situ* values of conductivity when poly-3'4'-DDTT deposition is conducted at 0.01 V s^{-1} indicates that the chemical-physical nature of the film obtained at 0.01 V s^{-1} during a single oxidative scan is practically the same as when oxidized poly-3'4'-DDTT is deposited cyclically in the same range of applied potential ($0 \leq E_{\text{appl}} \leq 0.9 \text{ V vs Ag/Ag}^+$).

In the case of poly-3'4'-DDTT it is then evident that the electrical conductivity depends on the kinetics of deposition. This because scan rate affects the current and, in cascade, the rate of

oxidative coupling as well as the rate of polymer deposition/precipitation. In particular, the mechanism of poly-3'4'-DDTT electrodeposition is characterized by the occurrence of polymer precipitation mainly when the polymer is in the neutral state, i.e. during the reverse scan of polymer neutralization in an oxidative cyclic voltammetry.[41,56,81] This implies that the electrodeposition conducted in a single oxidative scan, like in case of the experiments in Figure 2, represents the most unfavourable condition for obtaining a thick, compact layer of poly-3'4'-DDTT since there is no application of a reverse scan of neutralization during which polymer precipitation actually occurs. The closeness of the conductivities determined potentiostatically *ex situ* on a preformed film undergoing electrochemical *p*-doping and potentiodynamically *in situ* during electrodeposition in a single oxidative scan at the scan rate of 0.01 V s⁻¹ reveals that such a rate of potential scanning represents the optimum for the attainment of an oxidized poly-3'4'-DDTT film with relatively high quality in terms of electronic transport properties, i.e. with the largest conductivity achievable. In the potentiodynamic mode, consisting in a single oxidative scan in the present work, the formation of poly-3'4'-DDTT deposit occurs unavoidably when the products of polymerization are in the oxidized state.[51] This because at the potential of monomer oxidation, i.e. the initial step of coupling,[49] the products of monomer addition are subject to further oxidation for the possession of larger conjugation length.[71,72] At 0.01 V s⁻¹ the rates of formation the oxidized chains as well as their lengths allow the reach of local temporary concentrations in proximity of the electrode which are large enough to induce the precipitation of structurally regular compact films constituted by oxidized chains. At the optimum scan rate of 0.01 V s⁻¹ the corresponding volume yield is 1.12*10⁻² cm³ C⁻¹, i.e. an intermediate value the parameter η being proportional to the scan rate in case of poly-3'4'-DDTT electrodeposition (Table 1). Therefore, volume yield values larger and smaller than 1.12*10⁻² cm³ C⁻¹ (or, equivalently, scan rates larger and smaller than 0.01 V s⁻¹) afford poly-3'4'-DDTT deposits with worse conductivity properties with respect to the film attained at the intermediate scan rate of 0.01 V s⁻¹. At the slower scan rate of 0.001 V s⁻¹ the peak of current density is 3 μ A cm⁻² and the formation of a highly conductive bridge – a condition which is assumed to be satisfied when the polymer conductance varies linearly with deposition charge (Figure 2) – requires the consumption of at least 51.3 mC cm⁻² (vs 6.1 and 3.1 mC cm⁻² for bridge completion at 0.01 and 0.1 V s⁻¹, respectively). The relatively slow formation of the products of monomer and oligomer coupling allows the effective dispersion of the oligomeric species in solution with consequent loss of material in proximity of the electrodic substrate. This phenomenon would prevent the build-up of a sufficiently large concentration of chains (with correspondingly high lengths of conjugation) to overcome their limit of saturation near the electrode. The resulting low volume yield should not be considered real since it is a consequence of a great loss of material

due to the occurrence of back diffusion of the lighter products of coupling towards the bulk of the electrolyte. In fact, at the end of the coating process at 0.001 V s^{-1} the solution of deposition appeared deeply coloured in blue for the presence of a large amount of dissolved oligothiophenic species in the oxidized state.[119] This observation would indicate that these species did not precipitate completely at the moment of their formation. Another consequence of that is the attainment of a polymeric precipitate that is constituted by chains generally shorter in length and with lower extent of conjugation with respect to those forming the precipitates that are deposited at faster rates. The formation of poly-3'4'-DDTT deposits with chains having relatively short lengths of conjugation will provoke at the microscopic level the detriment of the intrachain charge transport capabilities with a deleterious impact on the overall conductivity.[120,121] This combination of observations can justify the relatively low conductivity of the film of poly-3'4'-DDTT grown at the lowest scan rate of 0.001 V s^{-1} .

When poly-3'4'-DDTT is grown at the highest scan rate of 0.1 V s^{-1} the conductivity of the resulting film is 25.1 S cm^{-1} (intermediate value) while the accompanying value of volume yield is the largest achieved here, i.e. $2.23 \cdot 10^{-2} \text{ cm}^3 \text{ C}^{-1}$ (Table 1). Under these conditions of electrodeposition, the formation of a polymeric conductive bridge between the two electrode bands is complete when the smallest amount of oxidative charge of 3.1 mC cm^{-2} is consumed. The latter value is determined from the intercept of the linear portion of the corresponding conductance curve (full line Figure 2). Given the linear proportionality of the current density peak to the scan rate (as typical of solid state electrochemical processes the rate determining step of which is surface confined)[122-124] for the process of poly-3'4'-DDTT potentiodynamic electrodeposition we observed the highest current density peak ($35 \text{ vs } 3 \mu\text{A cm}^{-2}$ for the slowest potentiodynamic scan at 0.001 V s^{-1}) when electrodeposition was conducted at the largest scan rate of 0.1 V s^{-1} . A high oxidative current brings about a relatively rapid accumulation of oligomeric species, i.e. the first products generated by monomer coupling, near the electrode. This situation, in turn, would favour the process of long chains formation near the electrode as well as their fast precipitation. Under these circumstances phenomena of oligomers dispersion in the oxidized state are not favoured. Different to slow scan rate electrosynthesis, at the end of fast and medium scan rate electrosyntheses the solutions of deposition did not appear blue-coloured. This fact is indicative of the lack (or event the total absence) of optically detectable amounts of oligomers in solution. Moreover, difficulties in achieving long chains do not arise at 0.1 V s^{-1} (this is different to the situation created by the passage of a low current density, *vide supra*). Such considerations are supported by the concomitant determination of the highest volume yield and lowest amount of “bridging” charge of deposition at the conditions imposed by a high potentiodynamic scan rate. On

the other hand, the efficacious process of deposit formation was not accompanied by the availability of a polymer with the highest electrical quality since the poly-3'4'-DDTT grown at 0.1 V s^{-1} presented an intermediate value of conductivity (25.1 S cm^{-1}) and not the largest one (that is 33.4 S cm^{-1} for the poly-3'4'-DDTT grown at 0.01 V s^{-1}). At the basis of this combination of findings for poly-3'4'-DDTT film grown at 0.1 V s^{-1} we consider the realization of a defective packing of chains (lower than those deposited at 0.001 V s^{-1} , *vide supra*) with consequent detriment of interchain and eventual interfiber charge transport capabilities.[120,125] The defective packing would be caused by the relatively fast process of deposition/precipitation at 0.1 V s^{-1} . On the other hand, we cannot completely exclude the eventual co-inclusion of larger amounts of solvents entrapped between the precipitating chains due to their faster formation and their faster aggregation with respect to the situations generated in front of the electrode (or at its surface) at 0.001 and 0.01 V s^{-1} . [126] Such a phenomenon would augment the volume yield (as verified, indeed), but at the same time would disfavour interchain electron hopping for the enlargement of the interchain spacing. The eventual occurrence of that would lead to the diminution of the electronic conduction properties in poly-3'4'-DDTT with respect to a precipitate that contains a lower amount of entrapped solvent.[120,125]

At the intermediate scan rate of electrodeposition (0.01 V s^{-1}) the peak of current density is $7 \mu\text{A cm}^{-2}$. At this rate the oxidized polymer bridges the double-band electrode when a charge density of 6.1 mC cm^{-2} has passed. The corresponding volume yield is $1.12 \cdot 10^{-2} \text{ cm}^3 \text{ C}^{-1}$ and the resulting film of poly-3'4'-DDTT displays the largest conductivity of 33.4 S cm^{-1} (Table 1). This finding allows to define the optimal conditions at room temperature for the preparation of poly-3'4'-DDTT with the best electrical properties at a given chemical composition of electrodeposition electrolyte. The product $\eta \cdot Q'$ gives the value of the critical thickness (h) the electrodeposit has to reach to form a conductive bridge between the two bands (Scheme 2). This thickness value is practically invariant with the scan rate being $h = 6.8 \cdot 10^{-5} \text{ cm}$ at the scan rate of 0.01 V s^{-1} and $h = 6.9 \cdot 10^{-5} \text{ cm}$ for the electrodeposits obtained at both 0.001 and 0.1 V s^{-1} . Such a result is important since it would prove that the conductive bridge sizes are not dependent on the scan rate of potentiodynamic deposition. Consequently, the differences in poly-3'4'-DDTT conductivity (or in the conductance of the polymeric bridge, Table 1) have not a geometrical origin but are related to the nature of the constituents of the electrodeposited film. This leads us to conclude that the scan rate of electrodeposition affects principally the chemical nature of poly-3'4'-DDTT electrodeposits and chain packing properties (in the oxidized state) rather than film density or compactness as verified here with the *in situ* analysis of the *p*-type electrical conductivity.

For the determination of *in situ* conductance during polymer growth the parameter of the consumed charge density (Q') comprises the charge of deposition and the doping charge since the electrolyte contains both monomer (the starting redox species) and supporting electrolyte. The latter provides the charge-compensating ions apt to counterbalance the electronic charge in the polymer and preserve its electroneutrality. The potentiodynamic mode of poly-3'4'-DDTT deposition implies that the anodic charge is partly consumed for the oxidative coupling of the reactive species (monomers and oligomers-either in solution or entrapped in the polymeric matrix)[127] and partly employed for doping (or oxidizing) those chains that are not longer involved in an electrochemical process of coupling under the actual conditions of deposition.[41] To have an idea of the order of magnitude for these two different destinies of consumed charge we performed a separated experiment of cyclic voltammetry with a fully grown film of poly-3'4'-DDTT in the neutral state when the electrolyte was monomer-free. Under these conditions only poly-3'4'-DDTT doping could occur while the process of oxidative coupling at the basis of polymer growth is not allowed. We found that poly-3'4'-DDTT exchanged reversibly 7 mC of doping charge when the deposition charge was 52 mC. This result indicates that only a small of fraction of the total charge (*ca.* 12%) is actually employed in poly-3'4'-DDTT doping during polymer potentiodynamic growth. Therefore, the observed linear increase of poly-3'4'-DDTT conductance with the logarithm of the consumed charge (Figure 2) is related to an increase of the extension of the front of a conductive layer (size effect) that has already reached its maximum conductivity and it must not be seen as a consequence of an increase of polymer conductivity in a preformed bridge.[45] The conductance profiles of Figure 2 are characterized by a sudden rise when electrodepositions are conducted at 0.1 and 0.01 V s⁻¹, while the electrodeposition at the lowest scan rate of 0.001 V s⁻¹ is accompanied by a very gradual increase of conductance. The two distinct trends of conductance (one for the two faster depositions and one for the slower deposition) are attributed to different kinetics of bridge formation. The observation of a sudden rise of conductance indicates that the formation and the completion of a conductive bridge constituted by a polymer at the state of maximum conductivity is not rate determining. On the other hand, the slow increase of conductance with the consumed charge, as observed for the electrodeposition at 0.001 V s⁻¹, indicates that the formation and the completion of a conductive bridge become rate determining at the lowest scan rate.

For poly-3'4'-DDTT the values of volume yield (Table 1) result generally one order of magnitude higher than polypyrrole grown galvanostatically.[75] This stems from the fact that the same amount of oxidative charge couples terthiophenic monomers each time and not single rings. In addition to that, the presence of the two long dodecyl chains in the starting monomer 3'4'-DDTT renders even

more voluminous the resulting polymeric precipitate with respect to the polymer containing the same number of heteroaromatic units but with no pending groups.

For poly-3'4'-DDTT the complete profiles of *in situ* conductance show that this parameter reaches a plateau with the consumed charge in proximity of the maximum value of applied potential (0.9 V vs Ag/Ag⁺), i.e. at the end of the single oxidative scan. Different to the case of poly-3-methylthiophene [75], the levelling off of poly-3'4'-DDTT conductance suggests that no chemical-physical degradation of poly-3'4'-DDTT occurs during its potentiodynamic growth within the applied potential range $0 \leq E_{\text{appl}} \leq 0.9 \text{ V vs Ag/Ag}^+$. This finding would prove that the so called PT paradox[74,128] is not taking place in the poly-thiophenic system here examined. The main reason for that is the employment of a terthiophene as starting monomer, i.e. a species that oxidizes at potential values which do not lead to the oxidative degradation of the corresponding products of coupling in the condensed state.[73,74] In this context the adoption of the potentiodynamic procedure that is under potential control appears a safe one for the electrodeposition of a conjugated polymer with stable conductivity.

During the potentiodynamic growth at 0.001 V s^{-1} poly-3'4'-DDTT reaches a plateau value of 2.8 S (Figure 3), which corresponds to the conductivity of 9.2 S cm^{-1} when the approximated formula

$$G \approx \frac{\sigma l}{\pi} * \ln \left(\frac{4b}{a} \right) \quad \{4\}$$

is adopted.[75] For calculating the conductivity of the polymer from the conductance plot of Figure 3 we considered the data range $\ln(Q') > 8$ using the following values of geometrical parameters: $a = 1.75 \text{ }\mu\text{m}$, $b = (w + a) = 51.75 \text{ }\mu\text{m}$ and $l = 0.2 \text{ cm}$.

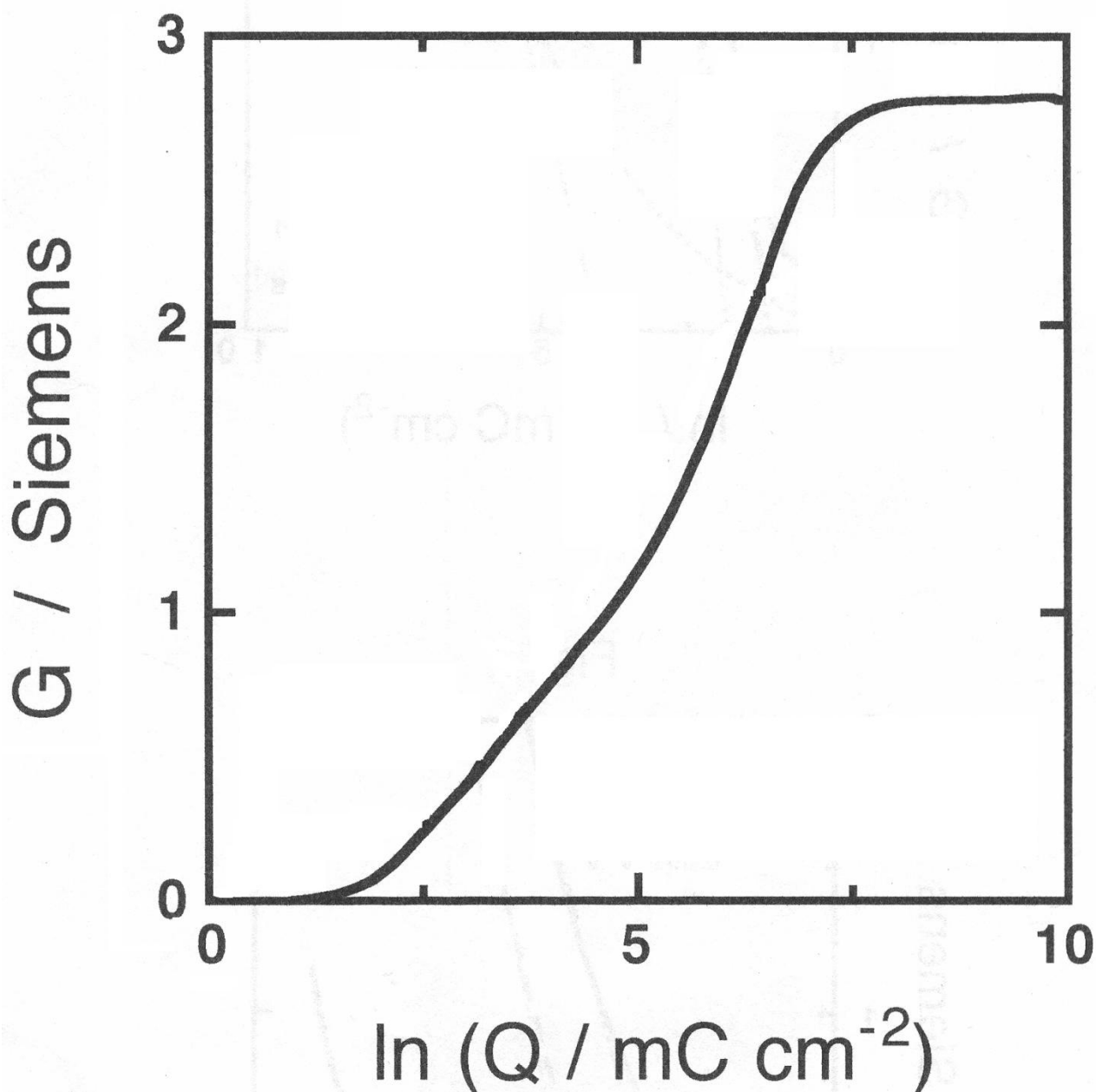


Figure 3. Variation of the conductance (G) of a poly-3'4'-DDTT film with the logarithm of the anodic charge during potentiodynamic oxidative electropolymerization. The profile has been recorded in conditions of quasi-homogeneous doping through the whole thickness of the polymeric film employing a very low scan rate (0.001 V s^{-1}). At the end of the experiment the conductance of the electrodeposited polymer reached a plateau of 2.8 Siemens.

At the higher scan rates of deposition also the conductance profiles of poly-3'4'-DDTT tended to level off with the consumed charge (not shown). For the conductance of the poly-3'4'-DDTT films electrodeposited at the scan rates of 0.1 and 0.01 V s^{-1} we determined, respectively, 6.9 and 9.1 S as plateau values. These corresponded to the conductivity values of 22.6 and 29.9 S cm^{-1} (Eq. 4) for the poly-3'4'-DDTT films deposited at 0.1 and 0.01 V s^{-1} , respectively. The values of

conductivity obtained from Eq.1 are systematically higher than the ones calculated through Eq.4 but their agreement can be taken as acceptable given the many approximations considered in the data treatment and the increasing importance of lateral growth upon increase of the consumed charge (this phenomenon is particularly influential in the range of application of Eq.4).[75]

Conclusions

The room temperature conductance of poly-3'4'-DDTT has been measured *in situ* with a double-band electrode when the polymer was grown potentiodynamically. In particular, poly-3'4'-DDTT was grown during a single oxidative scan in the applied potential range $0 \leq E_{\text{appl}} \leq 0.9 \text{ V vs Ag/Ag}^+$ employing three different scan rates (10^{-3} , 10^{-2} and 10^{-1} V s^{-1}). The profiles of the conductance vs anodic charge density presented a characteristic sigmoid shape that was indicative of the growth of a polymeric bridge in a highly conductive state and denoted poor lateral growth outside the inter-band space in the range of consumed charge. This type of measurements allowed the determination of the electrical conductivity and volume yield of deposition through the analysis of the conductance curves adopting the approach of conformal mapping. The volume yield increased with the scan rate and resulted generally high in comparison to other conductive polymers grown electrochemically due to the employment of a terthiophenic monomer (with bulky pending groups, i.e. the two dodecylic substituents of 3'4'-DDTT) and not a single unsubstituted heteroaromatic ring as building unit. The scan rate of poly-3'4'-DDTT deposition influenced the electrical conductivity (σ) of the resulting electrodeposits being found $12.9 \leq \sigma \leq 33.4 \text{ S cm}^{-1}$. The optimal conditions of deposition for the attainment of highly conductive poly-3'4'-DDTT are represented by the adoption of a scan rate of 10^{-2} V s^{-1} when the electrolyte composition was $c(3'4'\text{-DDTT}) = 2 \text{ mM}$, $c[(n\text{-C}_4\text{H}_9)_4\text{NClO}_4] = 0.1 \text{ M}$ (the supporting electrolyte) in the solvents mixture acetonitrile/benzonitrile (volume ratio: 4/1). Scan rate affected the electrical quality of the electrodeposits in terms of extent of conjugation length (a parameter controlling intrachain electronic transport) and packing properties (that, in turn, affect the interchain electronic transport), but showed scarce influence on the density and the compactness of the resulting electrodeposits. At high values of anodic charge density the conductance of poly-3'4'-DDTT reached a plateau value that depended on scan rate. Such a feature afforded a second way of calculating the electrical conductivity with an approximated formula that led to the systematic attainment of lower conductivity values with respect to the first method.

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