

Comparative Study of Isomeric Polyalkylterthiophenes with Regular Regiochemistry of Substitution: Characterization of Electrochemical Doping Process

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In this paper we present a systematic study of the effect of the substitution pattern in the starting monomers on the resulting properties of some electrodeposited polydidodecylterthiophenes. The compared characterization of p-doping processes in regioregular electropolymerized poly-3',4'- and 3,3''-didodecyl-2,2':5',2''-terthiophene is here reported for the first time. The in situ variations of the optical, magnetic, and electrical transport properties have been measured and correlated with the effects associated to the substituent position. An important result was the verification of absorption fine structures in the wavelength range $500 < \lambda < 620$ nm for the optical spectra of the electropolymerized polydidodecylterthiophenes thus confirming the typical features of regioregular polymers. Visible spectra and cyclic voltammeteries verified that poly-3,3''-didodecyl-2,2':5',2''-terthiophene possessed a more effective electronic conjugation with respect of the other isomer poly-3',4'-didodecyl-2,2':5',2''-terthiophene. On the other hand the latter polymer showed a higher value of the electronic conductivity (33 vs 21 S cm⁻¹). Such differences were discussed in terms of the effect of the substituent position on the polymers packing and the separation between chains.

Introduction

Despite of the great amount of studies on polyalkylthiophenes with regioregular chemistry of substitution^{1–11} due to the interesting properties of this class of materials,^{12–15} the direct comparison between the properties of polydialkyloligothiophenes electrochemically

synthesized from regioregular and symmetrical isomers is still lacking. In fact previous studies concerned mainly the effect of the substituent length,^{16–18} the separation between the substituents in the starting oligothiophenes,^{19–22} or the characterization of single symmetrical systems mainly based on the substitution pattern 3',4'-dibutyl-2,2':5',2''-terthiophene in the starting monomers.^{23–26} Such comparative characterization would represent a fundamental step for the direct evaluation of the effects due to the position of the substituents in isomeric regioregular starting monomers when the properties of the resulting electropolymerized systems are considered.

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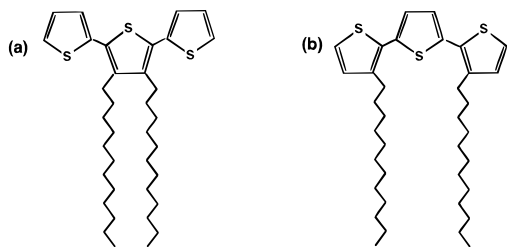


Figure 1. Structures of the starting monomers (a) 3',4'- and (b) 3,3''-didodecyl-2,2':5',2''-terthiophene (DDTT).

The optical, magnetic, electrical, and mass variations of the electropolymerized poly-3',4'- and 3,3''-didodecyl-2,2':5',2''-terthiophene (DDTT) upon electrochemical oxidation are here reported and results are compared for the two isomer polymers. The choice of dodecyl group as alkyl substituent in polyalkylthiophenes is motivated by the good properties of the resulting polymers in terms of structure planarity²⁷ and electronic conjugation.²⁸ Moreover such systems represent two elegant examples of electrosynthesized polyalkylterthiophenes with structurally homogeneous configuration²⁹ in which defective random coupling,³⁰ and undesirable head-to-head and tail-to-tail interactions²⁸ are dramatically decreased for the presence of a regioregular pattern of substitution in the starting monomer (Figure 1). In this perspective it will be demonstrated that the choice of a proper substitution pattern in the starting monomer can allow the advantageous electrochemical synthesis³¹ of structurally homogeneous polymers^{19,23} whose preparation is generally based on chemical routes.^{28,32–34}

Experimental Section

The electrochemical doping of poly-3',4'- and poly-3,3''-DDTT was made in the mixture acetonitrile (AN)/benzonitrile (BN) [volume ratio = 4:1] with tetrabutylammonium perchlorate (TBAP) 0.1 M as supporting electrolyte. Details on monomers preparation and electrochemical polymers synthesis are given respectively in refs 32 and 35. AN was purchased from Aldrich and it was dried by means of distillation over CaH₂ and P₂O₅. TBAP was purchased from Fluka and it was used as received. Poly-DDTTs were deposited onto working electrodes which varied with the kind of the experiment. The polymers were characterized both in the potentiodynamic and potentiostatic modes with a three-electrodes cell. A Pt wire was used as counter electrode in all measurements. The electrode Ag/AgNO₃ 0.01 M in acetonitrile was used as reference electrode³⁶ in all measurements but electron spin resonance (ESR) spectroelectrochemistry. In the latter case a silver wire was used as a quasi reference electrode (−0.25 V vs Ag/AgNO₃). In the text all potential values are referred to Ag/AgNO₃ 0.01 M in acetonitrile (0.34 V vs SCE). Electrochemical measurements

were performed with a PAR potentiostat (EG&G, model 362). The amount of polymer deposition charge ranged between 20 and 100 mC cm^{−1}. The electrochemical doping processes of the polymers were always run in N₂ atmosphere. The UV–visible absorption spectra of poly-DDTTs at different oxidation states of poly-DDTTs were taken in situ with a Perkin-Elmer spectrometer (model Lambda 15). Poly-DDTTs were electrochemically deposited onto indium tin oxide (ITO) for the spectral measurements; ITO electrodes were purchased from Balzers. The electrochemical cell for in situ UV–vis spectroelectrochemistry has been previously described.³⁷ ESR measurements were realized with a Bruker spectrometer (model ER100D x-band). The experimental details of in situ ESR spectroelectrochemistry are reported in ref 38. The in situ determination of polymers conductivity was made with a double-band electrode according to the experimental procedure described in ref 39. The evaluation of poly-DDTTs mass changes during electrochemical doping processes was accomplished with a homemade electrochemical quartz crystal microbalance (EQCM). The circuit of the EQCM resonator was built following the basic scheme of construction presented in ref 40. The digital monitoring of the quartz frequency was realized with a frequency counter from Hewlett-Packard (model 5316B). The calibration of EQCM was made by means of Ag deposition from the solution AgNO₃ 0.01 M + TBAP 0.1 M in AN. The conversion factor of the frequency variation into mass variation was 1.1 × 10^{−9} g Hz^{−1} as derived from the Sauerbrey equation.⁴¹ The working conditions in the EQCM experiments with poly-DDTTs allowed the direct use of Sauerbrey equation.⁴²

Results and Discussion

The cyclic voltammograms of poly-3',4'- and poly-3,3''-DDTT are shown in Figure 2a with the accompanying in situ variations of ESR signal (Figure 2b), electrode mass Δm (Figure 2c), and poly-3',4'-DDTT conductance S (Figure 2d). The oxidation of poly-3',4'-DDTT (poly-3,3''-DDTT) starts at $E = 0.50$ V (0.48 V). A single peak at $E = 0.71$ and 0.66 V, respectively, for poly-3',4'-DDTT and poly-3,3''-DDTT is present in the anodic scan of the voltammogram (Figure 2a), whereas two reduction waves appear with a broad shape in the reverse scan. The latter are approximately centered at $E = 0.72$ and 0.52 V for poly-3',4'-DDTT and $E = 0.52$ and 0.64 V for poly-3,3''-DDTT. The current trend in the anodic scan of the poly-DDTTs cyclic voltammograms is then not symmetrical with respect of the cathodic one. As a matter of fact only one single oxidation process is detected during the anodic scan because of the low wettability and the structural stiffness of polythiophenes in the pristine as-deposited state.³⁸ The potential value corresponding to the main oxidation peak is approximately the same for the two isomer poly-DDTTs with poly-3,3''-DDTT possessing the lowest value (Figure 2a). This would indicate comparable conjugation lengths when low amounts of charge ($Q_{\text{dep}} \leq 20$ mC) are deposited for both poly DDTTs.

The oxidation charge is not completely removed during the course of the cathodic sweep as calculated from the integration of the current in Figure 2a with

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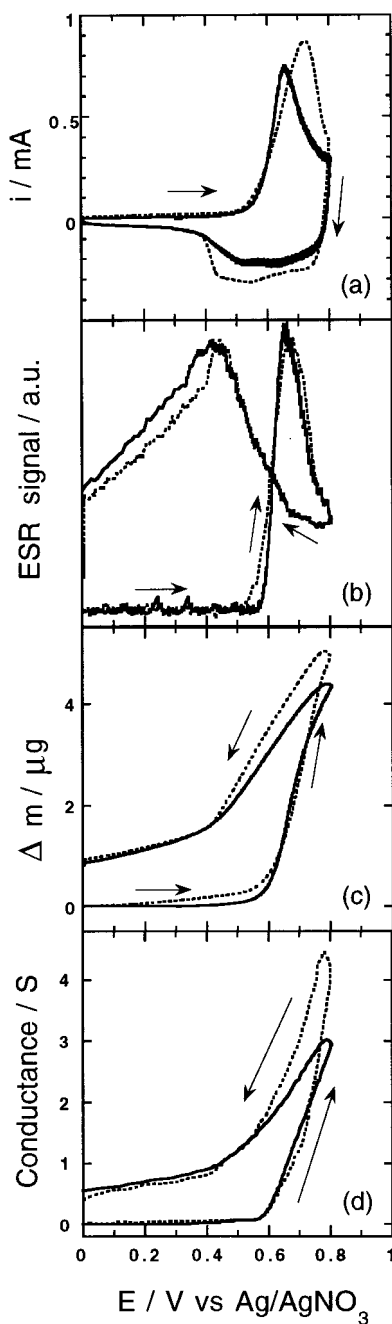


Figure 2. (a) Cyclic voltammety of poly-3',4'-DDTT (dotted line) and poly-3,3''-DDTT (full line) at 20 mV s⁻¹ (deposition charge 20 mC); corresponding (b) in situ variation of ESR signal, (c) EQCM response Δm , and (d) polymer conductance during a.

time (trapped charge: 0.63 and 0.45 mC, respectively, for poly-3',4'- and poly-3,3''-DDTT). This excess charge is associated with nonzero ESR signal (Figure 2b) and the trapping of mass (Figure 2c) detected at the end of the voltammogram (retained mass: 0.95 and 0.86 μg , respectively, for poly-3',4'- and poly-3,3''-DDTT). It has been found that Δm at the electrode is approximately linear with the exchanged charge Q as evaluated by the integral of the current with time from Figure 2a. The slope of the curve Δm vs Q is 1.5 and 1.9 $\mu\text{g mC}^{-1}$ respectively for poly-3',4'- and poly-3,3''-DDTT. The neutralization of the polymer charge during the oxidation process is then accomplished by the insertion of solvated perchlorate anions. The EQCM results (Figure

2c) give an effective mass of the exchanged species corresponding to one perchlorate anion and one (two) AN molecule(s) for poly-3',4'-DDTT (poly-3,3''-DDTT) as expected for polymers doped in polar solvents.^{38,43} In fact the slopes 1.5 and 1.9 $\mu\text{g mC}^{-1}$ correspond respectively to species with molecular weights 145 and 185 if each of these species carry one electronic charge. The sum of the masses corresponding to one perchlorate anion [MW (ClO_4^-) = 99.45] plus one (two) molecule(s) of acetonitrile [MW (CH_3CN) = 41.06] is 140.5 (181.6). Therefore is quite reasonable to conclude that the species inserted in poly-3',4'-DDTT (poly-3,3''-DDTT) is $\text{ClO}_4^- + (2)\text{CH}_3\text{CN}$. In the adopted conditions, the solvent is linked to the doping anion through an ion-dipole bond. The use of polar solvents is made necessary for the dissolution of the electrolyte and the solvation of the anion inside the polymer whose alkylic substituents are basically apolar. The elemental analysis of polyalkylthiophenes doped in analogous conditions verified the inclusion of solvated perchlorate anions in the polymeric matrix.^{44,45}

The ESR signal (Figure 2b) shows one sharp peak in the anodic scan at $E = 0.67$ V (0.65 V) and one broad scan at $E = 0.45$ V (0.42 V) in the cathodic scan of the applied potential for poly-3',4'-DDTT (poly-3,3''-DDTT). It should be noted that ESR signal does not disappear at the maximum value of the applied potential ($E = 0.80$ V). During the anodic scan the onset of the ESR signal growth is found at $E = 0.55$ V and varies linearly with the applied potential in the narrow range $0.55 \leq E \leq 0.65$ V for both polymers. In the cathodic scan, the ESR signal increases with an approximately exponential trend when E ranges between 0.80 and 0.50 V. In the potential range $0.00 \leq E < 0.55$ V the conductance S is null for both polymers (Figure 2d). The onset of a steep increase of S is detected when $E = 0.60$ V. In the range $0.60 \leq E \leq 0.80$ V, the variation of poly-DDTTs conductance with E is approximately linear. During the anodic scan the ESR signal reaches a maximum when poly-3',4'-DDTT exchanges approximately one-fourth of the total charge Q_{tot} (Figure 3a, full line). ESR signal does not extinguish when poly-3',4'-DDTT reaches the maximum level of doping ($Q/Q_{\text{tot}} = 1$). In the spanned range of E , poly-3',4'-DDTT conductance increases with Q/Q_{tot} according to a quasi-exponential law⁴⁶ (Figure 3, dotted line). The maximum ESR signal of poly-3',4'-DDTT is accompanied to a polymer oxidation state with intermediate conductivity. It should be noted that after reaching of the maximum ESR signal, the growth of conductance vs Q/Q_{tot} undergoes an acceleration. The oxidation state of poly-3',4'-DDTT with the maximum of conductance gives the lowest value of the ESR signal.

In the ESR signal vs Q/Q_{tot} curve for poly-3,3''-DDTT (Figure 3b, full line), a broad maximum is detected when $Q/Q_{\text{tot}} \approx 0.3$. The extinction of the ESR signal when poly-

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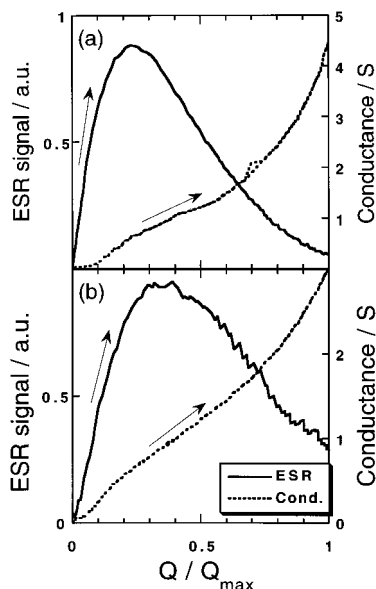


Figure 3. Variations of ESR signal (full line) and conductance (dotted line) with the ratio Q/Q_{tot} during the cyclic voltammetry of (a) poly-3',4'-DDTT and (b) poly-3,3''-DDTT.

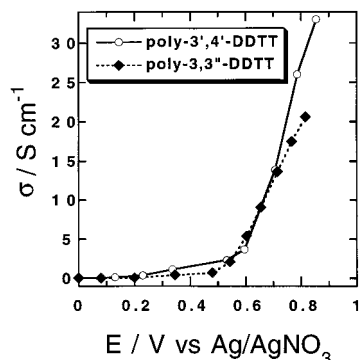


Figure 4. Conductivity σ variation of poly-3',4'-DDTT (O) and poly-3,3''-DDTT (◆) vs applied potential (potentiostatic measurement).

3,3''-DDTT is fully oxidized, i.e., $Q/Q_{\text{tot}} = 1$, is not observed. Moreover the ESR signal does not extinguish when the cycle is complete, being $Q/Q_{\text{tot}} = 0.15$ at the end of the cycle. The trend of the conductance vs Q/Q_{tot} is still characterized by the presence of a quasi-exponential regime (Figure 3b, dotted line). The minimum value of the ESR signal ($Q/Q_{\text{tot}} = 1$) corresponds to the poly-3,3''-DDTT state with the maximum conductance.

From these results one can conclude that the behavior of poly-DDTTs is characterized by the presence of at least two distinct states during the electrochemical oxidation process.^{47,48} One state, the low-doped state, can be identified by the fast increase of spin content and slow increase of electronic conductance with the doping level within the approximate limit of $Q/Q_{\text{tot}} < 0.25$ (Figure 3). It will be shown in Figure 4 that in this regime the conductivity σ also keeps low values ($\sigma \leq 5$ S cm⁻¹) varying at the slowest rate with dopant concentration. Such results lead to the conclusion that in

the low-doped state charge carriers possess spin and resemble the typical features of polarons.⁴⁹ Different from the ESR signal, the slope change of conductance vs Q/Q_{tot} occurs when the polymer is more than half-doped ($Q/Q_{\text{tot}} > 0.5$).

The second state (the highly doped state) is identified by the quasi exponential decay of ESR signal and the relatively fast increase of S with Q/Q_{tot} (Figure 3). The adding of dopant could then induce the magnetic coupling between charge carriers in order to minimize electrical repulsion.⁴⁹ The existence of a pure bipolaronic regime cannot be invoked in the highly doped state even if poly-DDTTs reach the maximum conductivity. This is because poly-DDTTs show non null intensity of ESR signal when $Q/Q_{\text{tot}} = 1$.^{50,51} In this regime it will be seen that the optical spectra are characterized by the decrease of the absorption in the whole visible wavelength range at very highly doped states (spectra 4 and 6 respectively in Figure 5a and 5b). The latter feature is consistent with the onset of a quasi-metallic behavior bringing about the diminution of the band gap.^{52,53} The existence of the high-doped state is located approximately in the potential range $0.7 < E < 0.8$ V as determined from Figure 2.

The measurement of poly-DDTTs conductivity σ is accomplished in the potentiostatic mode and the relative trends are shown in Figure 4. The values of σ do not depend substantially on the way of varying E , i.e., by increasing or decreasing E . The maximum values of poly-3',4'-DDTT and poly-3,3''-DDTT σ (respectively $\sigma_{\text{max}} = 33$ and $\sigma_{\text{max}} = 21$ S cm⁻¹) are attained at the upper limit of the potential range, i.e., $E = 0.80$ V.

The comparison of poly-DDTTs conductivities σ , from Figure 4, shows that the isomers have comparable σ values (σ_{max} is 33 and 21 S cm⁻¹ respectively for poly-3',4'- and poly-3,3''-DDTT in the fully oxidized state). This finding is consistent with the fact that σ is mainly controlled by the interchain hopping.⁵⁴ In fact the presence of the large dodecyclic substituents present in poly-DDTTs, provokes approximately the same separation among polymeric chains regardless of the relative position in the monomer structure. On the other hand, the highest value of σ for the poly-3',4'-DDTT is probably due to a better packing of the polymeric chains with respect to the other isomer due to preferred structural rearrangements during the oxidation process.⁵⁵⁻⁵⁷

The solid-state UV-vis spectra of poly-3',4'-DDTT and poly-3,3''-DDTT at different oxidation states are shown respectively in parts a and b of Figure 5. A single broad absorption centered at the wavelength $\lambda = 502$ nm is present in the spectrum of neutral poly-3',4'-DDTT (1, Figure 5a). When poly-3',4'-DDTT is fully oxidized (4,

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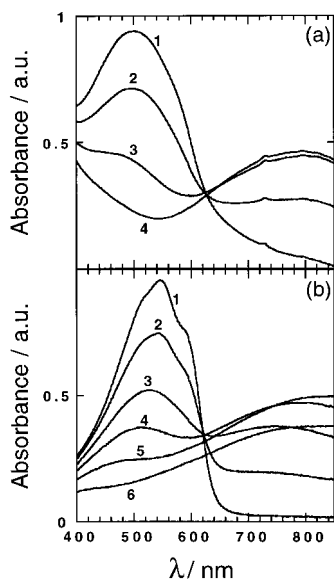


Figure 5. In situ optical spectra of (a) poly-3',4'-DDTT and (b) poly-3,3''-DDTT at different oxidation states (spectrum 1, neutral polymer; spectra 2, 3, 4(b), and 5(b), partially oxidized polymer; spectra 4(a) and 6(b), fully oxidized polymer). Both poly-DDTTs electrodes were rinsed with CHCl_3 before optical measurements ($Q_{\text{dep}} = 50$ mC at the end of electropolymerization).

Figure 5a), the new broad absorption peak is approximately centered at 796 nm. An isosbestic point can be identified at $\lambda = 630$ nm during the oxidation process of poly-3',4'-DDTT. The spectrum of neutral poly-3,3''-DDTT (1, Figure 5b) shows a fine absorption structure with one peak centered at 546 nm and two shoulders at 520 and 590 nm. The onset of neutral poly-3,3''-DDTT absorption is located at $\lambda = 640$ nm. The oxidation of poly-3,3''-DDTT provokes the lowering of the absorption in the range $400 \leq \lambda < 630$ nm (2–5, Figure 5b) and the appearance of a new broad absorption centered approximately at 850 nm when poly-3,3''-DDTT is fully oxidized (6, Figure 5b). At moderate doping levels (2–4, Figure 5b), optical spectra of poly-3,3''-DDTT are linked by the presence of one isosbestic point at $\lambda = 620$ nm. Taking into account the model of two-states system (low- and high-doped states)⁴⁸ as detected by the cathodic scan of the cyclic voltammetry (Figure 2a), in situ ESR, and electronic conductance measurements (Figure 3), in the low-doped state, the optical changes give rise to the formation of an isosbestic point (spectra 1–3, Figure 5a and 1–4, Figure 5b).⁵⁸ The comparison of the optical spectra of neutral poly-DDTTs in Figure 5 allows the analysis of the differences in the conjugation effectiveness. Poly-3',4'-DDTT has a lower value of λ_{max} in comparison with poly-3,3''-DDTT (502 vs 546 nm). This is representative of substantial differences in conjugation lengths and molecular ordering of the isomer polymers when electrochemical polymerization proceeds. Despite the fact that poly-3',4'-DDTT shows the highest conductivity in the oxidized state (Figure 4), thus indicating a better transport efficiency of the electronic charge with respect of poly-3,3''-DDTT, the latter isomer shows a larger extent of conjugation in the neutral state as determined by the value of λ_{max} in the optical spectra (Figure 5). This means that electrical conductivity involves primarily interchain interactions

of swollen systems,⁵⁹ whereas the optical properties of the neutral polymers concern mostly intrachain properties.⁵⁸ Moreover the regioregularity of the electropolymerized system²⁸ is not the only relevant point to take into account for the examination of the polymer electronic properties but the growth kinetic must also be considered.⁶⁰ In fact, it has been verified that the conjugation degree and the morphological order depend on thickness film regardless of regioregularity^{13,61} or regiorandomness⁶² of the resulting polymers.

In the present case the regioregularity of the resulting electropolymerized systems is warranted by the symmetrical pattern of substitution in the starting monomers DDTTs. On the other hand it is found that this condition is not enough for the attainment of an optical spectrum with fine structure⁶³ when poly-DDTTs grow thicker (Figure 5). In fact the lack of fine structure is verified with poly-3',4'-DDTT (Figure 5a), but not with the other isomer (Figure 5b). Such finding is not expected if one follows the criterion of the correspondence between regioregularity and optical fine structure.⁶³ Therefore other causes must be considered, e.g., molecular packing and chains planarity of the electrodeposited polyDDTTs for the explanation of the observed spectral phenomena which depend on the different regiochemistry of substitution. Similar to regiorandom polythiophenes which show generally a broad absorption peak centered at 480 nm³, the optical spectrum of neutral poly-3',4'-DDTT in chloroform (not shown here) presented an analogous bathochromic shift (~ 20 nm) with respect to neutral solid poly-3',4'-DDTT (spectrum 1 in Figure 5a). The latter qualitatively resembles the features of the spectra produced by these regiorregular systems but λ_{max} is relatively higher (500 nm) in poly-3',4'-DDTT. Therefore the degree of molecular ordering has a major extent in poly-3',4'-DDTT with respect to regiorandom systems.

Conclusions

The characterization of two regioregular polydidodecylterthiophenes concerned the determination of the changes in the electrochemical, magnetic, electrical, and optical properties upon electrochemical oxidation. The behavior of the isomers poly-3',4'- and 3,3''-didodecylterthiophene during p-doping was characterized by the existence of at least two distinct states differing for the variation of conductivity, ESR, and optical absorption with the amount of inserted charge. In the low-doped regime the conductivity increases in a relatively slow way, whereas ESR absorption increases in a fast way with the amount of inserted charge. In the high-doped state conductivity variation accelerates and ESR ab-

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sorption tends to extinguish. Strong charge trapping is verified in both polymers at the end of potentiodynamic electrochemical neutralization. The oxidation of polydidodecylterthiophenes brought about the intercalation of the perchlorate anion in the adopted conditions. Differences in optical absorptions of the neutral isomer polymers are ascribed to the different packing of the polymeric chains due to distinct kinetics of electrochemi-

cal deposition. Typical features of ordered regiochemistry are more evident in the optical spectra of poly-3,3''-didodecylterthiophene. Differences in conductivities for the isomer polymers are mainly determined by the volume and not by the relative position of the large dodecyl substituents in the polymeric chain.

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