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Electrochromic properties of poly(alkoxy-terthiophenes): an experimental and theoretical investigation

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Abstract Much effort has been made to synthesize novel compounds and enhance the optical properties of poly(terthiophenes). The electrochromic properties of poly(4,4''-dimethoxy-3'-methyl-2'-5',2''-terthiophene) (PDMMT) and poly(4,4''-dipentoxo-3'-methyl-2'-5',2''-terthiophene) (PDPMT) have been studied focusing on the differences in the alkoxy-group length. Theoretical calculations were employed to elucidate the structural and thermodynamic stability of the monomers and dimmers. The results showed that in this type of thiophenes large alkoxy chains assist positive charge dispersion through hyperconjugative effect. Thus, PDPMT is thermodynamically more stable than PDMMT in the oxidized state, leading to better electrochromic stability and optical memory.

Keywords Poly(terthiophenes) · Electrochromic properties · Theoretical calculations

Introduction

The spectroelectrochemical properties of electrochromic materials have attracted much attention due to the possibilities of their application in the optical industry. Besides their exceptional stability, thiophene derivatives can be easily synthesized at a low cost and provide reasonable contrast in multiple colors. These features make them good candidates for use in displays, mirrors, and smart windows [1]. By the comprehension of the state-of-the-art some research groups have devoted efforts to the synthesis of polythiophenes and their

derivatives leading to tailored materials. These studies allowed the so-called monomer engineering. In this sense, studies have shown that polythiophenes containing a side chain alkoxy substituent show the advantage of easy doping [2]. The alkoxy group in the 4,4'' position also favors dissolution and allows electrochemical polymerization [3]. Results in the literature showed that poly(alkoxy/alkyl-terthiophenes) are substituted thiophenes with electrochemical and spectroelectrochemical properties strongly dependent on the alkoxy chain length. This dependency affects the absorption spectra and redox properties [4].

From a theoretical viewpoint, polythiophene (PT) has rapidly become subject of considerable interest, and has been considered a model for the study of charge transport in conducting polymers (CP), mainly due to the existence of a non-degenerate ground state, its high environmental stability (doped and undoped states), and structural versatility [5].

The higher oxidation potential of thiophene compared to bithiophenes and terthiophenes induces electrochemical degradation on the final electropolymerized film. Recently, this problem was circumvented by extending the conjugation length of the monomer, resulting in a significant decrease in oxidation potential [6]. Therefore, polymers generated from terthiophenes possess a higher degree of structural order than those of polymers synthesized from thiophenes or bithiophenes [7]. The literature reports on the conformational properties of substituted bithiophenes [8, 9], terthiophenes, and longer oligothiophenes [10]. The results show that the substitution of one methyl group at positions 4 or 5 of bithiophene has no effect on the potential energy surface, but the substitution at position 3 has a noticeable consequence [8]. Moreover, these substitutions can affect the excitation energy E_{gap} , which determines the intrinsic properties (electronic and optical) of conjugated materials. In addition, planar distortions and interchain distances affect the excitation energy of the oligothiophene systems to some extent [11].

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Computational quantum chemical calculations are a powerful technique for the detailed study of molecular structures [12, 13]. The entire set of structural parameters (bond lengths and angles) as well as the molecular energy, which provides information on the relative stability of different species, can be determined by this procedure. Unfortunately, the application of computational chemistry to macromolecules such as proteins and polymers is still restricted to classical methods, i.e., molecular mechanics. Problems that require explicit consideration of the electronic structure have to be dealt with in fragments of the macromolecule due to the large computational cost of solving Schrödinger's equation for such systems. Despite this approximation, the information obtained from electronic structure calculations may be of great value in understanding their macroscopic behavior. Amid this knowledge lies the exciting aspiration of foreseeing the successful structure-to-property relationship, which may lead to effective tailoring procedures. Undoubtedly, substantial progress would arise through the molecular engineering dominium associated with other powerful knowledge, such as nanotechnology.

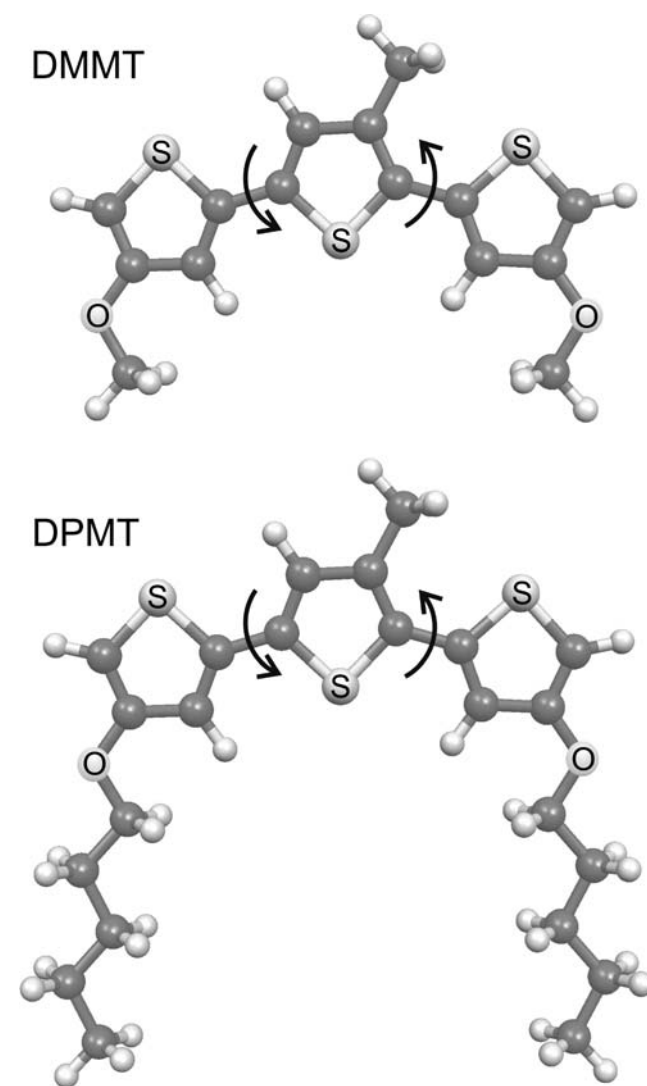
Regarding the number of recent papers dealing with electrochemical, electrochromic, photoelectrochemical, and photovoltaic properties of thiophenes and their derivatives, little attention has been devoted to the theoretical-empirical relation [14–19]. Hence, this paper discusses the electrochemical and electrochromic properties of poly(4,4''-dimethoxy-3'-methyl-2'-5',2''-terthiophene) and poly(4,4''-dipenthoxy-3'-methyl-2'-5',2''-terthiophene) thin films as a function of theoretical calculation outcome based on structural dissimilarities.

Materials and methods

The synthesis, purification, and characterization of the monomers 4,4''-dimethoxy-3'-methyl-2'-5',2''-terthiophene (DMMT) and 4,4''-dipenthoxy-3'-methyl-2'-5',2''-terthiophene (DPMT) were reported in previous papers [20, 21]. All the reagents and solvents used in this work were from Aldrich Chemical. Films of pDMMT were electrochemically prepared by two cycles of cyclic voltammetry (CV) using a 3×10^{-3} mol L⁻¹ solution of DMMT and DPMT and a 0.1 mol L⁻¹ solution of tetrabutylammonium perchlorate (TBAP) in an acetonitrile/dichloromethane (3:1 v/v) mixture. The potential was scanned between -0.2 V and 1.0 V (vs. Ag|AgCl) with a scan rate of 20 mV s⁻¹ at 30°C. Deposited film thickness was measured using a Tencor Alpha Step 200 Profilometer. Electrochemical experiments were carried out with an AUTOLAB potentiostat/galvanostat, model PGSTAT 30 (EcoChemie). A three-electrode electrochemical cell with indium/tin oxide (ITO-glass), (area = 1.0 cm² and surface resistivity 20Ω/square) as a working electrode, Pt wire as a counter-electrode, and Ag|AgCl were used as reference.

Films of PDMMT and PDPMT deposited on ITO-glass were cycled in the range from -0.2 V to 1.0 V (vs. Ag|AgCl) with a scan rate of 20 mV s⁻¹ using a Pt wire as a counter-electrode and a 0.1 mol L⁻¹ free monomer solution of TBAP in acetonitrile. Chronoamperometric analyses were carried out with double potential steps of -0.2 and 0.9 V (vs. Ag|AgCl) for 15 s each potential at different temperatures. Concerning the standard deviations of the electrode potential with temperature change, compensation was achieved by normalization procedures according to Ives and Janz [22].

Spectroelectrochemical measurements in the vis—NIR region were carried out using a 0.1 mol L⁻¹ solution of TBAP in acetonitrile, an Ag|AgCl electrode as a reference, ITO-glass sheets (area 1.0 cm², surface resistivity 20Ω/square) as working electrodes and a Pt wire as a counter-electrode. Spectroelectrochemical measurements were carried out by placing ITO modified elec-



Sch. 1 Structures of 4,4''-dimethoxy-3'-methyl-2',5',2''-terthiophene (DMMT) and 4,4''-dipenthoxy-3'-methyl-2',5',2''-terthiophene (DPMT)

trodes into the sample compartment of a diode array spectrophotometer (Hewlett-Packard 8453) and switching the applied potential by using a FAC200A potentiostat/galvanostat. The absorbance spectra of PDMTT and DPMT films were recorded at different polarization potentials: 0.2, 0.1, 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 V (vs. Ag|AgCl).

The electrochromic properties of PDMTT and DPMT films deposited onto ITO-glass electrodes were evaluated through chronoamperometric experiments with simultaneous acquisition of transmittance spectra using a 0.1 mol L⁻¹ solution of TBAP in acetonitrile as an electrolyte. Stability was tested by performing 1,400 square wave double potential steps at -0.2 and 0.9 V for 15 s at each polarization. This chronoamperometric experiment permits the evaluation of the life cycle and optical contrast ($\Delta\%T$), and response time. Transmittance data were recorded at 570 nm.

Theoretical calculations were performed with the Gaussian 98 [23] program suite. The structures were optimized using the RHF (ROHF for the radicals) method along with the minimal STO-3G basis set. Frequency calculations were carried out to characterize the structures as minima and to determine thermodynamic properties. The ZINDO [24] procedure was used to determine electronic transitions.

Results and discussion

Theoretical calculations were performed for DMMT and DPMT (monomers and dimmers) to obtain information about the stability of the oxidized and reduced states aiming a better comprehension of the structure-to-optical-property relation, which in this case were extrapolated to the polymers. In essence, theoretical calculations allowed us to find approximate solutions for Schrödinger's equation for polyelectronic systems. The energy eigenvalues might then be compared to provide an estimation of the relative stability of each species. Nevertheless, electronic structure methods generally use the Born-Oppenheimer approximation, in which the nuclei are held fixed throughout the calculations; therefore, the results furnished by this approximation neglect nuclear motion. The latter contribution may be taken into account through the calculation of vibrational frequencies, from which we can determine the

Table 1 Thermodynamic parameters calculated for the redox process

	ΔG_{298}°	ΔH_{298}°	ΔS_{298}°	ΔE_{SCF}^a
DMMT	99.271	97.493	-5.963	99.631
DPMT	97.522	95.772	-5.869	97.924
PDMTT (dimmer)	211.288	205.478	-19.486	208.684
PDPMT (dimmer)	206.011	199.892	-20.521	203.131

$$(\Delta G_{298}^{\circ} = G_{ox} - G_{red}/\text{kcal/mol}, \Delta H_{298}^{\circ} = H_{ox} - H_{red}/\text{kcal/mol}, \Delta S_{298}^{\circ} = S_{ox} - S_{red}/\text{cal/molK})$$

^a Electron-electron, electron-nucleus, nucleus-nucleus

Table 2 Entropy-contributing motions

	Contribution to ΔS			
	Vibrational	Translational	Rotational	Electronic
DMMT	-19.457	-0.029	0.000	0.000
DPMT	-20.498	-0.022	0.000	0.000

thermodynamical quantities, Gibbs free energy, enthalpy and entropy, among others, with the help of statistical thermodynamics. These values are compiled in Table 1 for the oxidation process of the dimmers and monomers of DMMT and DPMT. Scheme 1 shows the terthiophenes monomer structure and how the inter-ring torsion angle is defined.

Comparing the monomers, the entropy variation is only slightly different, precluding us from doing further analysis. The difference increases to a significant level (1.04 kcal/molK) for the DPMT dimmer, which presents higher entropy variation.

The kind of motions that contribute to the entropy were also examined, Table 2, and the data show that the entropy is essentially vibrational. In addition, calculations showed that the DPMT dimmer has 336 vibrational modes, while that of DMMT has only 192. Therefore, if the same perturbation type (e.g. oxidation) is imposed on DMMT and DPMT, it is expected that the effect of entropy variation on the polymers will be more intense on the species with higher probability of propagating the perturbation, i.e., on DPMT (with the penthoxy side group). Despite the entropic contribution, the theoretical results show that the stability of the reduced form relative to the oxidized one is essentially enthalpic, and that the oxidized structure of DPMT is always more stable than that of DMMT. The difference increases as one goes from the monomer to the dimmer, suggesting that a further increase in the stability of the reduced form should be observed for the polymer. Some important information presented in Table 1 is the self-consistent field energy (SCF), which includes electron-electron, electron-nucleus and nucleus-nucleus interaction energies, but disregards any kind of nuclear motion, vibration, translation, or rotation. Considering the SCF energy alone, we observe that DPMT is again more stable and that the energy difference (ca. 5 kcal/mol) is practically the same as that obtained for ΔG_{298}° . Therefore, the different behavior of the two polymers should be dictated by pure electronic and nuclear interaction energies. Moreover, the greater stability of the oxidized state of DPMT relative to the same state of DMMT may be rationalized in terms of electronic delocalization, since the larger alkoxy chain in DPMT helps to disperse the positive charge through hyperconjugative effects [12, 13]

Table 3 presents the electronic transitions (ground to the first excited state) calculated for the reduced and oxidized forms (monomers and dimmers). In particular, the studies of electronic transfer processes allow esti-

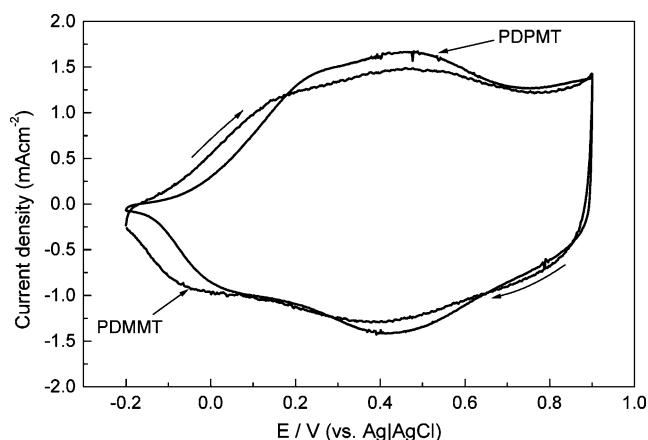
Table 3 Excitation energy ($E_{\text{transition}}$) of DMMT and DPMT monomers and dimmers for oxidized and reduced species

	$E_{\text{transition}}$ (red. state), nm (eV)	$E_{\text{transition}}$ (oxid. state), nm (eV)
DMMT	356.25, (3.4803)	555.15, (2.2333)
DPMT	356.18, (3.4809)	538.18, (2.3038)
dimer-DMMT	432.12, (2.8692)	643.50, (1.9267)
dimer-DPMT	432.66, (2.8656)	647.97, (1.9134)

mating the contributions related to intramolecular process propagation without the complications arising from interchain hopping during excitation [25]. Thus, it is possible, in principle, to study long range electronic transfer processes by knowing the relative distances between molecules and their orientations [26].

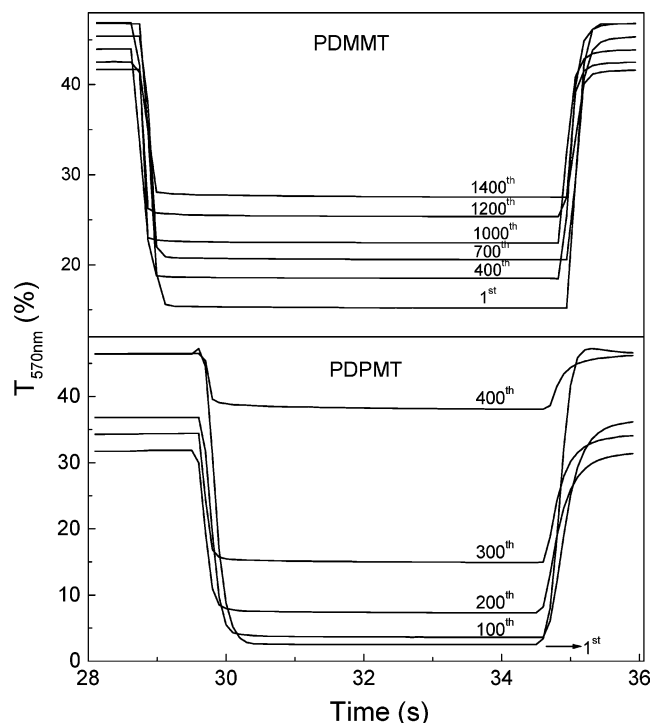
Considering the $E_{\text{transition}}$ of the dimmers (to which the data are extrapolated for the polymers, in this case), the data in Table 3 agree with the experimental results, i.e., the transition energy corresponding to the dimmers are lower than that of the monomers. In addition, comparing the data of excitation energy between reduced and oxidized states, the difference of energy between DMMT and DPMT is larger in the oxidized state. We suggest that the local chain torsions that stabilize the cation are more effective in the oxidized state and that the interchange from the reduced to oxidized states involves a structural reorganization. Due to the long side chain, the steric hindrance in DPMT is larger than in DMMT, which leads to a more difficult structural reorganization.

In the experimental investigation, thin PDMMT and PDPMT films were electrochemically polymerized and characterized by cyclic voltammetry sweeping the potential from -0.2 V to 0.9 V (vs. Ag|AgCl), Fig. 1. The occurrence of two redox peaks was observed, with the redox couples appearing at ca. $0.16/-0.05$ V and $0.47/0.38$ V to PDMMT and ca. $0.26/0.0$ V and $0.46/0.41$ V

**Fig. 1** Cyclic voltammogram of electropolymerized PDMMT and PDPMT. Synthesis solution was 0.1 mol L^{-1} TBAP and $3 \times 10^{-3} \text{ mol L}^{-1}$ DMMT or DPMT in acetonitrile/dichloromethane. Film coverage geometric area was 1.0 cm^{-2} and ca. 60 nm thick with electropolymerization at 30°C

to PDPMT. This result revealed two processes (three species), but could not identify them. However, the formation of polarons and bipolarons is probably involved, but such result cannot be referred only to the polaron-bipolaron formation, because during undoped-to-doped transition several effects give rise to redox and/or capacitive currents (mainly the inhomogeneous structure of the film, crosslinking, microporosity, etc.). According to the literature, the bipolaron model is more generally accepted [27, 28]. Ideally, the formation of thermodynamically stable multiple diionic states is assumed (bipolarons) during the ionization processes associated with local geometric chain distortion. At high doping levels, there is a preferential formation of bipolarons and for lower doping levels there is polaron formation. Concerning the voltammetric shape, reversible electrode reactions present anodic and cathodic peak potentials with a difference (k) of $0.0592/n$, where n is the number of electrons involved in the half-reaction [29]. For the two polymers studied, the difference between anodic and cathodic peaks of PDMMT is closer to k , evidencing a more reversible electrode reaction than for PDPMT, which agrees with the predicted theoretical calculations.

Figure 2 shows the optical contrast as a function of electrochromic cycles by applying successive double potential steps (-0.2 V and 0.9 V vs. Ag|AgCl) with simultaneous acquisition of the optical transmittance at 570 nm . The first electrochromic cycle indicates that

**Fig. 2** Optical contrast at 570 nm of PDMMT and PDPMT films during double potential step experiments between -0.2 V and 0.9 V (vs. Ag|AgCl). The film coverage geometric area was 1.0 cm^{-2} and ca. 60 nm thick with electropolymerization at 30°C

coloring has a faster kinetics than bleaching. For PDMMT, the average optical bleaching response time is 0.4 s and for coloring, 0.6 s; the optical contrast ($\Delta\%T$) (first cycle) is 39% and after 1,400 electrochromic cycles $\Delta\%T=17\%$. For PDPMT, these values are 0.6 s (bleaching), 0.7 s (coloring), $\Delta\%T=44\%$ (first cycle), and $\Delta\%T=9\%$ (400th cycle). The slower color change kinetics of PDPMT suggests a more complex structural reorganization caused by the steric hindrance of the pentoxy group. In addition, the larger stability of PDMMT to redox cycles can be assigned to its higher reversibility, which agrees with the theoretical results.

The current stabilization kinetics, which can be used to infer about the dynamics of the structural movements, was studied at different temperatures through chronoamperometry, Fig. 3. The chronoamperometric curves for PDMMT and PDPMT evidenced a faster current stabilization at high temperature. A distortion toward a structure of bithiophene and terthiophene at oxidized state extending over the whole molecule is produced by ionization [19]. Based on the fact that interchange between oxidized and reduced states involves a structural reorganization, the increase in temperature provides energy to overcome the rotational energy barriers, which is more effective in the case of PDMMT.

Absorption spectra in Vis-NIR range, Fig. 4, show the absorption of PDMMT and PDPMT at successive

doping levels. The reduced forms of PDMMT and PDPMT present absorbance maxima (Abs_{MAX}) at ca. 570 nm and 580 nm, respectively, corresponding to an intense blue coloration. The oxidation potential applied to both PDMMT and PDPMT is accompanied by a gradual decrease in absorbance intensity at Abs_{MAX} , simultaneously to a displacement of Abs_{MAX} to shorter wavelengths (blue shift). This fact is assigned to the slightly distancing between HOMO and LUMO levels at the expenses of the polaron/bipolaron formation. Delocalization of maximum absorption from reduced to oxidized state toward short wavelength also indicates that species with long chains are oxidized first. As the doping level is increased, a sub-gap absorption grows at the expense of the polaronic transition, as evidenced by the band located in the NIR region [30].

Conclusions

The electrochromic properties of PDMMT and PDPMT are strongly dependent on the length of the alkoxy-group. The alkoxy side groups have electron-donating properties and steric hindrances that lead to influences on optical and electronic properties at different ratios by different conformational structures. Due to the large

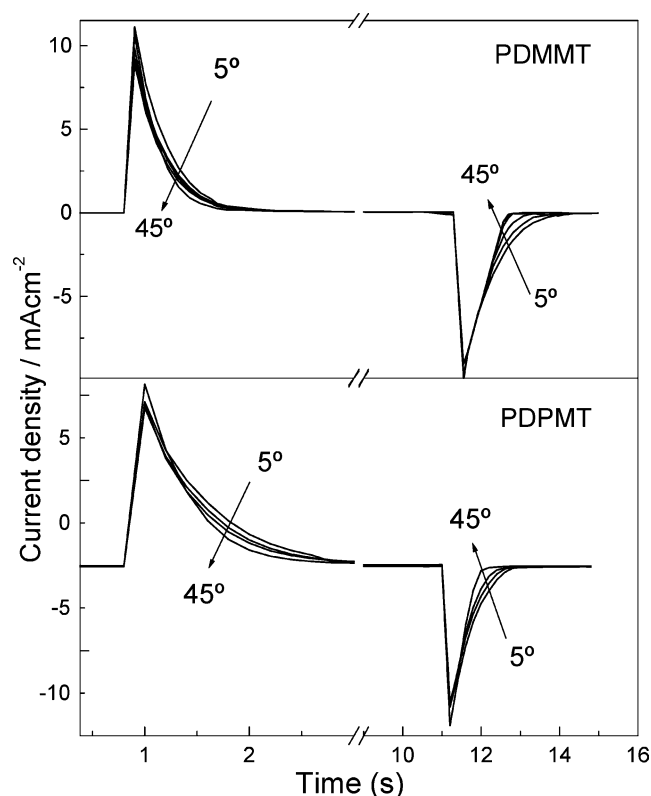


Fig. 3 Chronoamperogram of PDMMT and PDPMT films polarized at 0.9 V and -0.2 V recorded at different temperatures. The film coverage geometric area was 1.0 cm^{-2} and ca. 60 nm thick with electropolymerization at 30°C

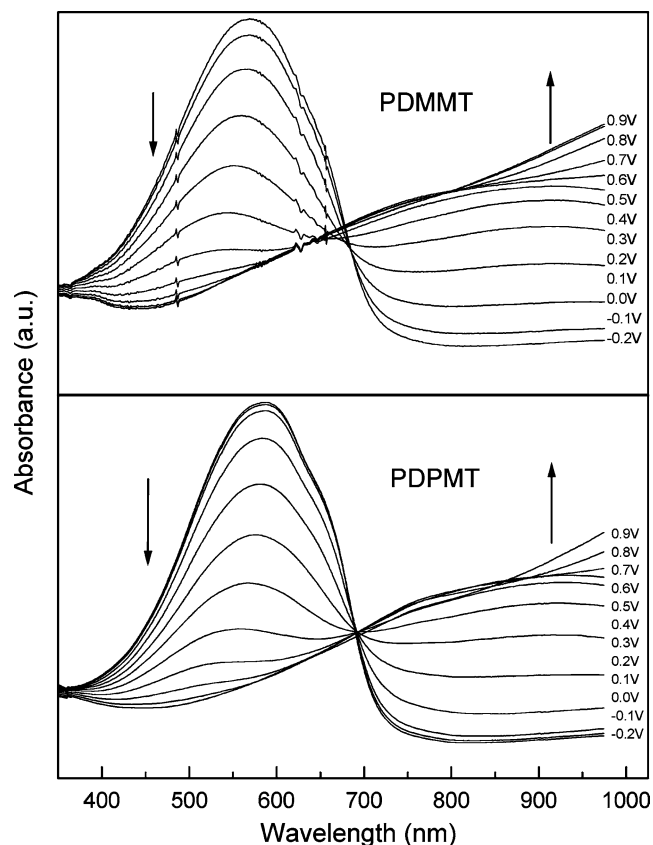


Fig. 4 Vis-NIR spectra of PDMMT and PDPMT films polarized at different potentials. The film coverage geometric area was 1.0 cm^{-2} and ca. 60 nm thick with electropolymerization at 30°C

alkoxy groups of PDPMT, structural reorganization through reduced and oxidized states is hindered, leading to a lower reversibility in the redox processes, and therefore to losses in coulombic efficiency. The theoretical calculation proved to be a very important tool, providing information on the structural and thermodynamic feature of the polymers that could be used in the monomer engineering seeking better and specific properties.

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