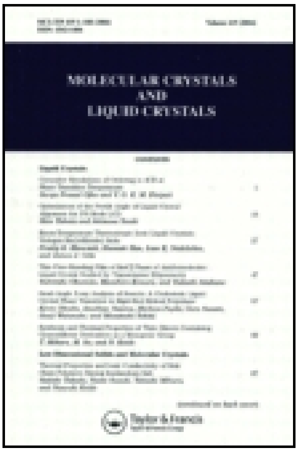

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Electrochemical and Optical Properties of Poly(3-Methylthiophenes) Electrosynthesized by 3,3′-, 3,4′- and 4.4′-Dimethyl-2.2′-Bithiophene

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ELECTROCHEMICAL AND OPTICAL PROPERTIES OF POLY (3 - METHYLTHIOPHENES) ELECTROSYNTHESIZED BY 3,3'-, 3,4'- AND 4,4'-DIMETHYL-2,2'-BITHIOPHENE

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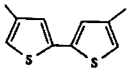
ABSTRACT 3,3'-, 3,4'- and 4,4'-dimethyl-2,2'-bithiophene are used as starting molecules for electrochemical polymerization of poly(3-methylthiophenes). The resulting polymers show different optical properties, interpreted on the basis of the conformation of the starting dimers determined by force field MMP2 calculations.

INTRODUCTION

We report a comparative study [1] of the electrochemical and optical properties of the poly(3-methylthiophenes) electrosynthesized starting from 4,4'- 3,4'- and 3,3'-dimethyl 2,2'-bithiophenes **I**, **II** and **III**, which can be viewed, respectively, as the result of tail-to-tail, head-to-tail and head-to-head α,α' coupling of two 3-methylthiophene units.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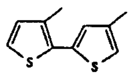
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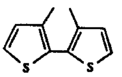

(III)

I, **II** and **III** were prepared by nickel-phosphine complex catalyzed Grignard coupling and characterized by ^{13}C NMR. A MMP2 force field theoretical study was carried out on **I**, **II** and **III**, aimed at gaining information on the relationship between the conformation and the optical absorption properties of these compounds, to use as a guide-line in the interpretation of the behaviour of the corresponding polymers.

RESULTS

A) Theoretical characterization of dimers **I**, **II** and **III**.

Table I shows conformational energies (*E, kcal* mol^{-1}), inter-ring twist angles ($\omega°$) and relative populations (*p%*) of **I**, **II** and **III** evaluated by MMP2 force field calculations for two different values of the dielectric constant (1.5 and 5.0, the latter being very close to the value for chloroform).

TABLE I. Conformational energies, inter-ring twist angles and relative populations of **I**, **II** and **III** for two different values of the dielectric constant.

		ω^a	$E_{1.5}$	$p_{1.5}$	$E_{5.0}$	$p_{5.0}$
I	*Cis*	0	19.4	23	17.8	84
	Trans	±27	19.1	77	19.2	16
II	*Cis*	0	22.7	1	21.0	30
	Trans	±38	20.6	99	20.8	70
III	*Cis*	±35	29.3	0	27.9	0
	Trans	±46	21.9	100	22.6	100

a) Deviation from the total mean plane

B) Electrochemical and optical characterization of polymers electrosynthesized from dimers **I**, **II** and **III**.

Poly(3-methylthiophenes) were electrosynthesized from **I**, **II** and **III** dimers on conductive TO electrodes by cyclic voltammetry (CV) at 50 mV s^{-1} between 0 and 1.2 V up to ca. 50 mC cm^{-2} in acetonitrile (ACN) - 0.5 M $LiClO_4$ and $1 \cdot 10^{-2}$ M dimer concentration. All polymers can be driven from undoped to doped states repeatedly with high contrast in colour. The electronic spectra in the visible and near ir regions of the undoped polymers and doped at different values of injected charge, recorded *in situ* in ACN-0.5M $LiClO_4$ at different applied potentials after that the equilibrium charge was reached, are shown in figure 1. These polymers show different optical properties: the maximum absorption of the undoped forms (π–π^* interband transition) varies from 2.95 eV (polyIII) to 2.58 eV (polyI) and to 2.43 (polyII), indicating different effective conjugation lengths of the polymers. Note that the evolution of the spectra of polymer polyIII is unusual: the absorption peak of the π–π^* transition does not shift towards the higher energies as the bipolaron bands increase (the bipolaron states coming in the gap are taken from the valence and the conduction band edges so that a widened bandgap is expected).

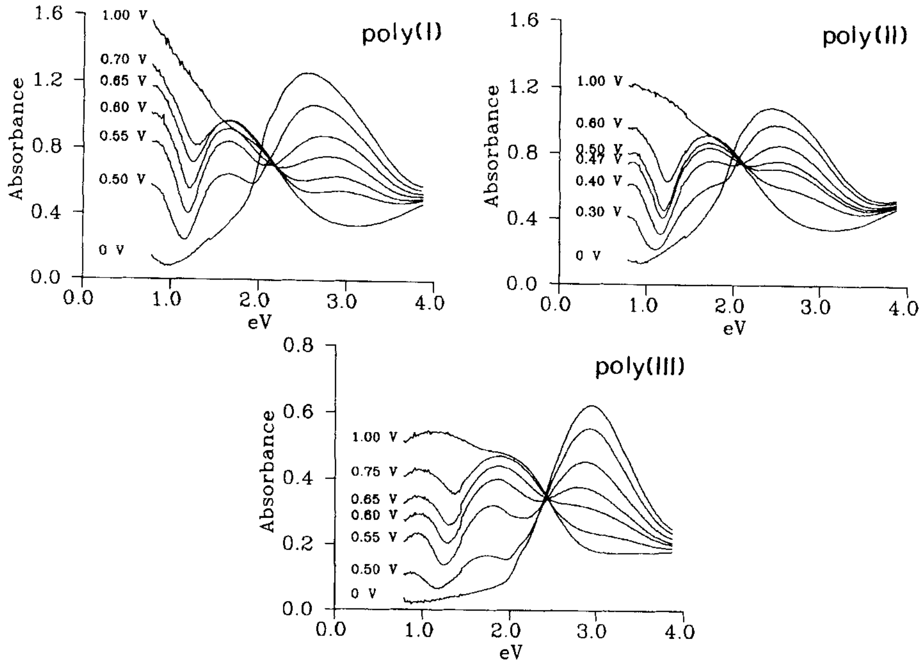


FIGURE 1. Evolution of the electronic spectra of poly(3-methylthiophenes) during electrochemical doping. All potentials are related to SCE.

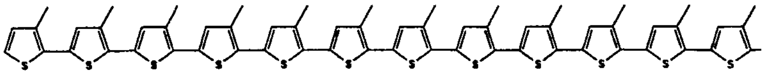
The colour contrasts when the polymers are switched from undoped to doped (at 1 V) states are reported in table II, where are also listed optical and electrochemical data of the starting molecules and of the polymers: the wavelengths of the maximum absorption (λ_{max}) in ACN-$LiClO_4$ of the dimers and of the undoped polymers, the oxidation potentials (E_{ox}) of the dimers and of the undoped polymers evaluated by oxidation peaks of CV in ACN-$LiClO_4$ at 50 and at 10 mV s^{-1} respectively, and the absorbance (A) of the maximum absorption of the undoped form of the polymers, as a measure of the polymerization yield.

TABLE II. Electrochemical and optical data of dimers **I**, **II** and **III**, and of the corresponding polymers.

	dimer		polymer				
	λ_{max} (nm)	E_{ox} (V)	λ_{max} (nm)	E_{ox} (V)	A	colour undoped	colour doped
I	311	1.21	480	0.74	1.25	orange-red	blue
II	299	1.22	510	0.55	1.05	red	blue
III	268	1.32	420	0.69	0.65	yellow	violet-blue

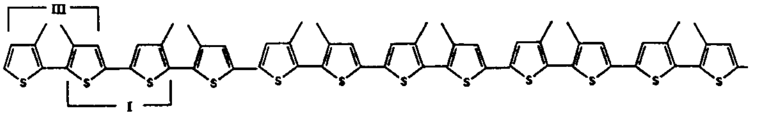
DISCUSSION

Our data show that poly(3-methylthiophenes) with significantly different optical properties may obtained starting from **I**, **II** and **III** dimethyl-2,2'-bithiophenes. The polymer from dimer **II** shows the highest λ_{max} value (λ_{max} = 510 nm), and, moreover, the value is very close to that of the polymer obtained starting from 3-methylthiophene (λ_{max} 530 nm), albeit electrosynthesized in different conditions. Of the three dimers only **II** is an unsymmetrical molecule, and like 3-substituted thiophenes, can link head-to-head, head-to-tail or tail-to-tail, leading to different sequences of 3-methylthiophene units. However, the 5- and 5'- positions of **II** are in the same relation as the 2- and 5-positions of 3-methylthiophene, and since it has been demonstrated that polymerization of 3-substituted thiophenes results in predominantly α,α' head-to-tail coupled rings [2], the fact that the λ_{max} values of polymers from the **II** dimer and from the monomer are very close indicates that polymer from **II** is the head-to-tail version of poly(3-methylthiophene), as shown below:



(1)

The dimers **III** and **I** lead *via* α,α- coupling to linked 3-methylthiophene sequences with the same substituent pattern except for chain ends, and the sequence is the stereoregular head-to-head / tail-to-tail version of poly(3-methylthiophene), as shown below:



(2)

The λ_{max} values of poly**I** and poly**III** are 480 and 420 nm, respectively. The fact that both polymers have a lower λ_{max} than that of poly**II** is explained assuming that sequence (2) has a less planar conformation than sequence (1), owing to the presence of head-to-head linkages, which force the molecule markedly out of planarity. In fact, force field calculations (table 1) show that while head-to-tail and tail-to-tail linkages are conformationally mobile (either planar or slightly out of planarity depending on the medium), head-to-head linkages are rigidly trans and strongly tilted, independent of the medium.

The large λ_{max} difference between poly**I** and poly**III** may be due to α,β' mislinkages adverse to conjugation in the latter. Indeed, in dimer **III** the β positions are free, whereas in dimer **I** they are not. However, it cannot be excluded that also conformational factors -implying a greater degree of planarity of poly**I** than poly**III**- contribute to the fact that poly**I** has a larger λ_{max} than poly**III**. Indeed, the conformational preferences of sequence (2) are not necessarily the same when it results from dimer **I** or from dimer **III**, as the growth of poly**III** leads to the formation of tail-to-tail junctions, whereas the growth of poly**I** leads to formation of head-to-head junctions.

In addition the unusual behaviour observed - on increasing the doping level - for the absorption peaks of the π–π^* transition of poly**III** but not of poly**I**, could be explained in terms of different conformations of sequence (2) for the two polymers. In fact, the reason why the absorption peak of the π–π^* interband transition of poly**III** does not shift towards higher energies as its intensity decreases, may be due to the fact that the whole chain of this more tilted polymer relaxes upon doping towards a more coplanar conformation. This evolution could also explain why, even if the λ_{max} value of the undoped form of this polymer is low, the conductivity of the doped form is high, as reported in reference 2.

ACKNOWLEDGMENT

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