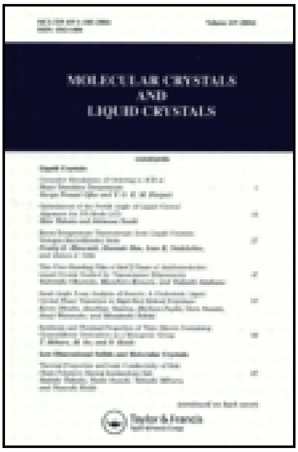

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: A. Bolognesi , M. Catellani , S. Destri , W. Porzio , C. Taliani & R. Zamboni (1990): Synthesis and Characterization of Polydithienothiophenes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 259-266

To link to this article: http://dx.doi.org/10.1080/00268949008036050

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 259-266
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Printed in the United States of America

SYNTHESIS AND CHARACTERIZATION OF POLYDITHIENOTHIOPHENES

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Abstract
We have designed and synthesized polydithieno[3,4-b:3',4'-d]-thiophene (PDTT) which has good conductivity, low energy gap and a spectral window of transparency. The doped and undoped polymer exhibit an electrochromic effect in the visible spectrum range.

INTRODUCTION

The scientific field of organic conducting polymers is ten years old and has catalyzed a wide interest. Recently it was recognized that these materials may have large non linear optical effects due to their delocalized π-electron system[1]. The development of conjugated polymers as useful new materials, in both the organic electrical and non linear optic fields, depends on the capacity to control the physical properties of the polymers.

Experimental and theoretical studies[2,3] of the relationship between the molecular structure and the electronic properties can guide the chemical design of new polymeric materials. In the field of conducting polyheterocycles we have seen that a modest modification of the chemical architecture of the monomer strongly affects the charge transport properties of the polymer[4]. The molecular characteristics required in order to impart good electrical and specific optical properties are:

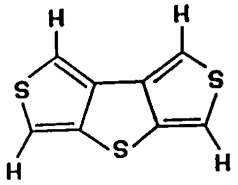
a) extended π-electron conjugation in the polymer backbone (regular enchainment, no chemical defects);

b) good mobility of the charge carriers (wide bandwidth of the HOMO band);

c) low energy-gap (the modulation of this property can give both intrinsecally conducting polymers, without the need of doping, and materials with a suitable spectral window of transparency).

The electrochemical polymerization of suitable monomers can give materials with controlled chemical architecture. In fact, a great number of polyheterocycles have been electrochemically prepared and they are a very relevant class of conducting polymers. With this in mind we have designed the monomer molecule: dithieno[3,4-b:3',4'-d]thiophene (DTT) (fig.1).

FIGURE 1



An increase of the π-electron delocalization is achieved by the fusion of three aromatic five-membered rings in β position with respect to the lateral thiophene moieties. This type of condensation (ß position) is probably the origin of the low energy gap of the polymer. In fact Wudl and al.[5,6] have shown that polyisothianaphtene, in which a thiophene ring is condensed in a β position with benzene, has an energy gap of 1.1 eV. A theoretical investigation of the geometry and the electronic properties of this polymer have confirmed that the geometry of the polyisothianaphtene produces a low π-π* transition energy with respect to the polythiophene.

EXPERIMENTAL

PolyDTT was prepared via electrosynthesis[7] in a two-compartment cell at room temperature with platinum or ITO electrodes, with a constant current of 1 mA/cm^2. The solvent was acetonitrile, the monomer concentration was 0.03 M, and we used $LiClO_4$ (0.1 M) as electrolyte. During the polymerization the oxidation potential remained constant at 1.04 V. The electrical conductivity, measured by the four probes technique, is 1 $S\cdot cm^{-1}$. It was performed in situ with an electrode test-pattern made of four gold electrodes separated by 33 µm deposited on a silicon substrate.

CHARACTERIZATIONS

The UV-Vis-NIR spectra of the polymer at different doping levels are reported in fig.2 .

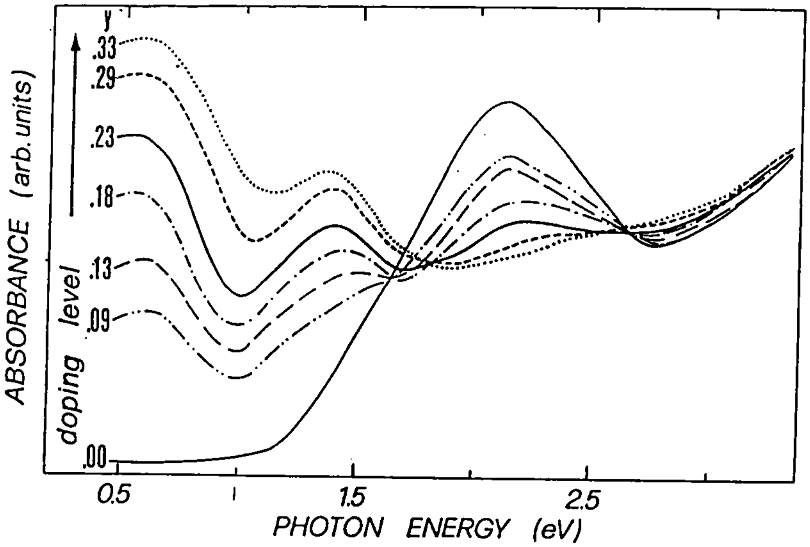


FIGURE 2 In situ UV-Vis-NIR spectra of PDTT at different doping levels.

The spectroscopy was performed in situ by applying a constant current of 0.1 mA/cm^2 for different times in a sealed electrochemical cell with acetronitrile, $LiClO_4$, and the neutral polymer as anode.

The neutral polymer has a strong absorption band due to a π-π^* transition with a maximum of 2.1 eV. The band-gap value of the polymer is 1.1 eV, which is, along with polyisothianaphtene, the lowest band-gap among conducting organic polymers. The π-π^* absorption band decreases with increase of the dopant level and two new absorption bands appear in the the spectra at 0.83 and 1.4 eV. These bands are evidence of the bipolaron formation and are characteristic for the conducting polyheterocycles.

A strong electrochromic effect between the conducting and the insulating polymers can be observed. While the reduced (undoped) polymer is opaque, the oxidized (doped) material is colourless and semitransparent. This reversible electrochromic effect has the maximum variation in transmission in the green range of the visible spectrum corresponding to the maximum in the human eye sensitivity.

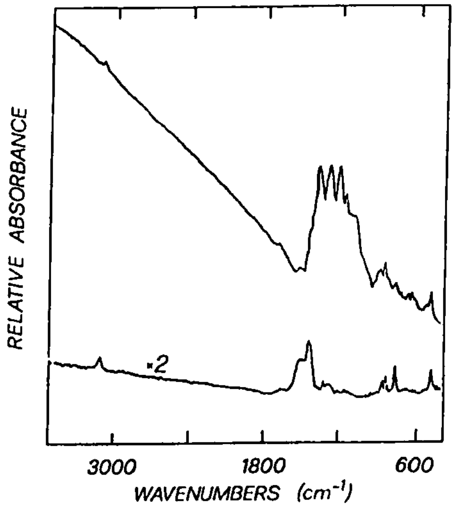


FIGURE 3 FTIR spectra of doped (upper curve) and undoped (lower curve) PDTT.

In fig.3 are shown the FT-IR absorption spectra of the polyDTT films grown on silicon substrates in the undoped and doped state. The conducting polymer shows a series of intense doped induced bands (DIB) in the 1100 - 1500 cm^{-1} spectral range. This behaviour is shown by other conducting polymers based on fused thiophene rings, and it is characteristic of the charge carriers.

The DTT monomer has, in principle, four possible points of electrical attachment. Different types of enchainment are possible in the polymer.

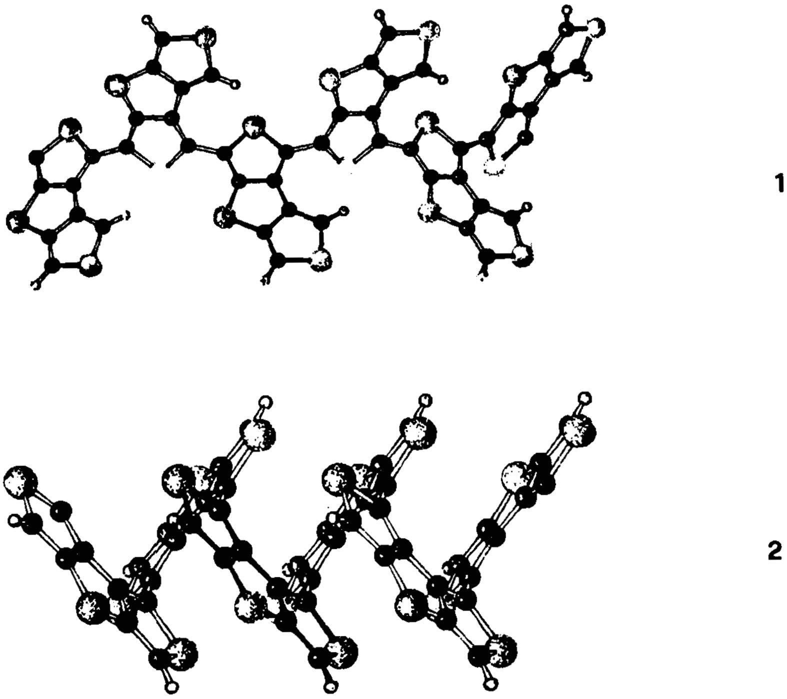


FIGURE 4 Optimized conformations of PDTT for enchainments 1 and 2.

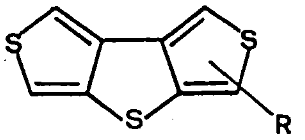
A limitation of the possible configurations is given by the evidence of bipolaron presence in the electronic spectrum of the doped polyDTT. In fact a polymer with bipolarons as charge carriers has a ground state in which aromatic and quinoid valence-bond resonance structures have comparable weight.

Only two types of enchainment give a low energy quinoid resonance structure as shown in the figure 4. In order to choose the correct configuration we have investigated the structure of both monomer and polymer, and we have performed molecular modelling calculations of the two possible conformations with the aim of establishing which is the best. On the basis of the monomer structure and on Allinger's potentials we have calculated the minimum energy conformation for the two enchainments.

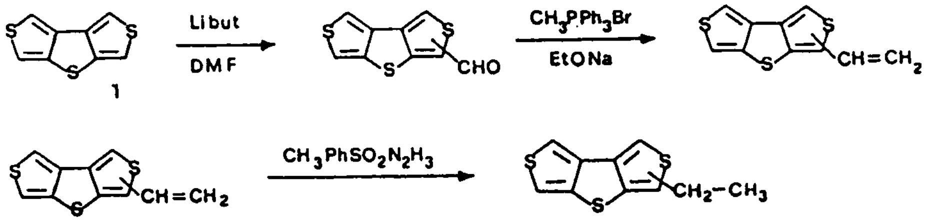
Enchainment 1 produces quasi planar chains stacked at a distance of about 3.5 Å. Enchainment 2 gives a chain in which two adjacent monomers form a dihedral angle of 77°. Enchainment 1 is largely to be preferred as it produces more effective overlap of π-electrons because of the reduced deviation from planarity.

SUBSTITUTED POLYDITHIENOTHIOPHENES

With the aim of producing a regular polymer enchainment we have synthesized two dithienothiophenes. The synthesis of the monomers is the following:



R = C_2H_5 ; C_2H_3



Both the monomers 1 and 2 give polymers by electrosynthesis, but their electrical behaviour is very different. The electropolymerizations were performed at room temperature with platinum or ITO electrodes at a constant current of 0.5 mA/cm^2. The monomer was dissolved in acetonitrile (0.03 M) with $LiClO_4$ (0.1 M) as electrolyte.

During the electropolymerization of the monomer 1 the oxidation potential rapidly increases. The grey polymeric film doesn't change its colour when the polarity of the electrodes is inverted. This behaviour is usual for insulating polymers. The electrosynthesis of polymer 2 produces a blue-violet film, and the oxidation potential remaines constant at 1.04 V (vs. SCE). During the de-doping process the colour of the film shifts from blue to grey. This polymer is very sensitive to oxygen, in fact the material rapidly changes its colour and the conductivity decreases under air exposure.

Figure 5 shows the UV-Vis-NIR spectra of the doped and undoped polymer 2.

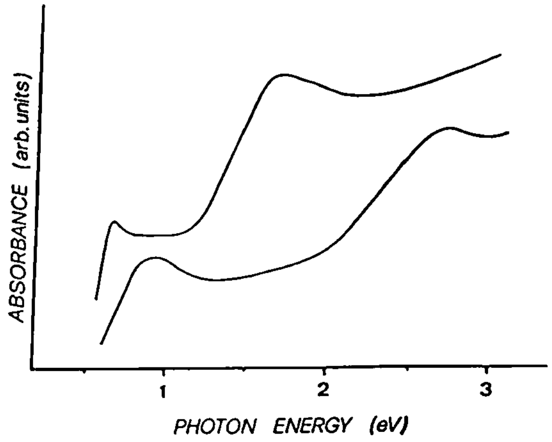


FIGURE 5 UV-Vis-NIR spectra of polymer 2 in the doped (upper curve) and undoped (lower curve) form.

A preliminary interpretation of the spectra can be the following : the neutral polymer has the π-π* transition at 2.7 eV and the conducting polymer has two bands at 1.7 and 0.8 eV, probably due to the bipolarons.

CONCLUSIONS

We have designed and synthesized a monomer giving by electrosynthesis a conducting polymer transparent in the visible spectrum, with a low band-gap. We have synthesized two substituted polydithienothiophenes and our next step will be the production of soluble conducting polydithienothiophenes, possibly in thin films, and the study of their electrooptical properties.

The authors wish to thank Mr. M.Mascherpa and Mr. A.Rossini for technical assistance

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