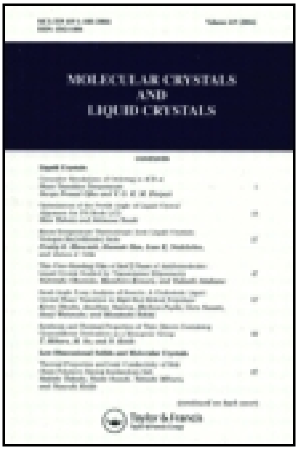

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Optical, Electrical and Electrochemical Characterization of The Doped Polydithienothiophene

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To cite this article: P. Di Marco , M. Mastragostino & C. Taliani (1985): Optical, Electrical and Electrochemical Characterization of The Doped Polydithienothiophene, Molecular Crystals and Liquid Crystals, 118:1, 241-244

To link to this article: http://dx.doi.org/10.1080/00268948508076217

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 241-244
0026-8941/85/1184-0241/$10.00/0

Printed in the United States of America

OPTICAL, ELECTRICAL AND ELECTROCHEMICAL CHARACTERIZATION OF THE DOPED POLYDITHIENOTHIOPHENE.

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INTRODUCTION

Electrochemical preparation has been recently shown to be a suitable method for obtaining a certain number of conducting heterocyclic aromatic polymers such as polypyrrole[1] and polythienylene[2]. The most attractive characteristic of the electrochemical approach is that the doping is simultaneous with the polymer preparation. We describe the electrochemical synthesis, electrical and optical properties of a new doped polymer, poly DTT polydithieno (3,2-b;2',3'-d) thiophene) shown in Figure 1, which because of the large delocalized Π electron orbitals[3] and the intrinsic planarity of the monomer[3] tend to favour the conjugation of the Π electron by reducing the rotational disorder along the polymer backbone. The electrochemical reduction to the undoped state has been also investigated.

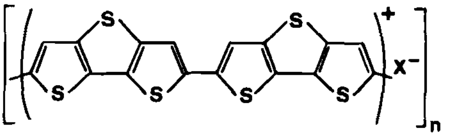

FIGURE 1 Idealized structure of doped poly DTT where $X^- = PF_6^-, ClO_4^-$.

ELECTROSYNTHESIS OF DTT POLYMERS DOPED WITH ClO_4^- AND PF_6^-.

The electrochemical polymerizations were performed at constant current (0.5 ÷ 1 mA cm^{-2}), by means of a galvanostat, on Pt and on SnO_2 coated electrodes, in degassed and anhydrous ($[H_2O] < 1.10^{-4}$ M) electrolytic medium involving methylene chloride, DTT (2.10^{-3} - 1.10^{-2} M) and the supporting salt MX 0.1 M ($M^+ = N(Bu)_4^+$; $X^- = ClO_4^-$, PF$_6^-$, at 288 K. The used cell had separated compartments. The polymer films were generated on Pt at = 1.2 V and on SnO$_2$ at = 1.4 V vs. SCE. The film thicknesses were controlled by the electrolysis time and typically varied between 0.1 μm and 1 mm.

The composition of the doped polymers determined by elemental microanalysis is: (C$_8$H$_2$S$_3$)X$_{0.5}$, where X is the dopant: ClO$_4^-$, PF$_6^-$.

Electrical Properties.

Electrical measurements on the powder, scratched off the electrode, were performed on compressed pellets at room temperature. The electrical contacts on both sides of the pellet were obtained by means of vacuum deposition of Al, or by painting with colloidal graphite. The resistivity was determined by applying a voltage across the sample and measuring the current flow. The typical conductivities are 1.10^{-2} and 3.10^{-3} S cm^{-1} for (DTT$_2^+$ PF$_6^-$)$_n$ and (DTT$_2^+$ ClO$_4^-$)$_n$ respectively.

ELECTROCHEMICAL GENERATION OF UNDOPED POLYMERS.

The feasibility of the electrochemical reduction of the polymers to undoped state has been tested by cyclic voltammetry (Figure 2), and the polymers in the neutral state have been prepared.

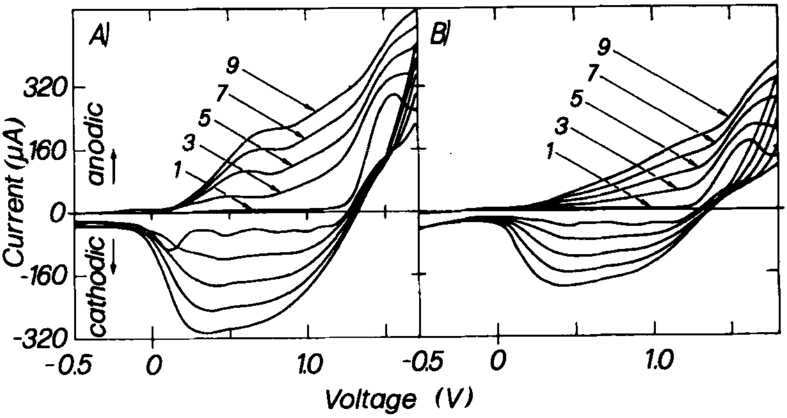

FIGURE 2 VC (.2V s^{-1}) on Pt for continuous cycles from negative to positive potentials. DTT = 2x10^{-3}M; A)NBu$_4$ClO$_4$ 0.1M; B)NBu$_4$PF$_6$ 0.1M.

The polymers generated in the oxidized doped state were, thereafter, electrochemically reduced, in the same electrolytic medium, to undoped neutral state at constant current ($I=-.2 - -1mA\ cm^{-2}$). The electrolysis time was chosen so that the charge involved in the reduction was 20% of the charge relative to the oxidation process.

OPTICAL PROPERTIES.

The mid-IR spectrum of a $(DTT_2^+\ PF_6^-)_n$ polymer in KBr is shown in Figure 3.

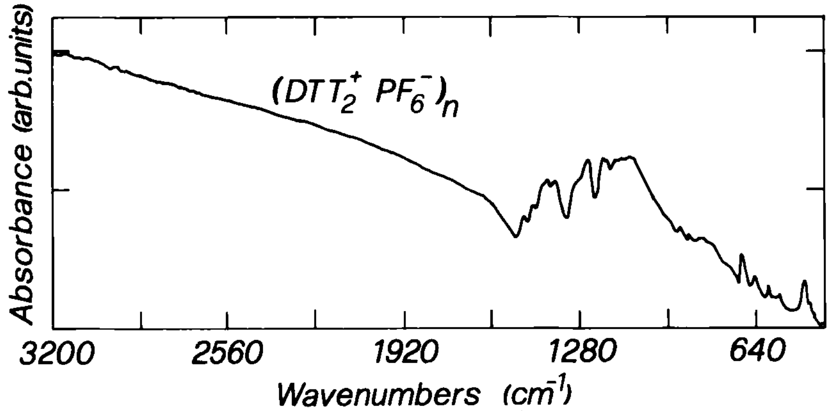

FIGURE 3 FT-IR mid-IR spectrum of $(DTT_2^+\ PF_6^-)_n$ polymer in KBr pellets.

The overall general features parallel in many respects the polythiophene spectrum[4]. Most of the bands are broadened as a result of the poor crystallinity of the material and are generally located at lower frequencies with respect to the characteristic frequencies of DTT. The rising continuum on the high frequency side of the spectrum is assigned to free carrier absorption.

The dramatic difference of the visible and near IR absorption of the (ClO_4^-) doped polymer compared to the undoped polymer is shown in Figure 4. The lowest electronic absorption band of the undoped polymer centered at 460 nm possesses a remarkable bandwidth of ~10.000-12.000 cm^{-1} which characterizes the widely delocalized Π electron system. A vestige of this band remains in the doped polymer spectrum which is marked by the wide free carrier absorption in the near IR.

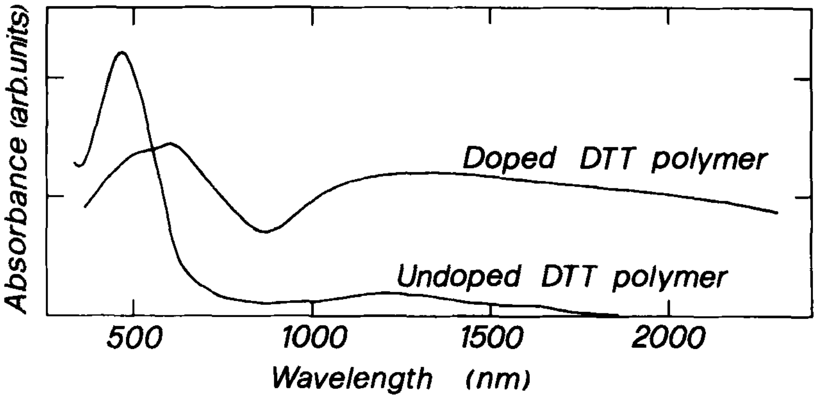

FIGURE 4 Visible and near IR spectrum of doped and undoped DTT polymers.

ACKNOWLEDGMENT.

This work has been supported by the Consiglio Nazionale delle Ricerche of Italy, Progetto Finalizzato "Chimica Fine e Secondaria". We thank Mrs. S. Rossini and Dr. R. Degli Esposti for helpful technical assistance.

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