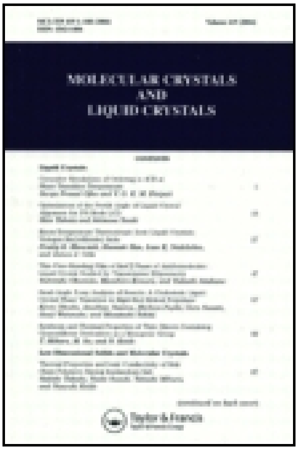


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Novel Organic Conductors: Effect of Structure On Band Gap

Fred Wudl [a], Masao Kobayashi [a], Nick Colaneri [a], Mark Boysel [a] & Alan J. Heeger [a]
[a] Institute for Polymers and Organic Solids, University of California, Santa Barbara, California, 93106, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: Fred Wudl, Masao Kobayashi, Nick Colaneri, Mark Boysel & Alan J. Heeger (1985): Novel Organic Conductors: Effect of Structure On Band Gap, Molecular Crystals and Liquid Crystals, 118:1, 199-204

To link to this article: http://dx.doi.org/10.1080/00268948508076211

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 199-204
0026-8941/85/1184-0199/$15.00/0

Printed in the United States of America

NOVEL ORGANIC CONDUCTORS: EFFECT OF STRUCTURE ON BAND GAP

FRED WUDL, MASAO KOBAYASHI, NICK COLANERI, MARK BOYSEL AND ALAN J. HEEGER
Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106, U.S.A.

Abstract The physical properties of a new polymeric conductor are presented. Because the band gap was reduced to ca. 1 eV, the material becomes transparent when highly doped since absorption is pushed into the infrared region of the spectrum upon doping.

INTRODUCTION

In a very simplified way, a significant contribution of poly(thiophene)'s semiconductor gap (Eg = 2eV) is attributable to the nondegeneracy of electronic structures A and B (Figure 1).

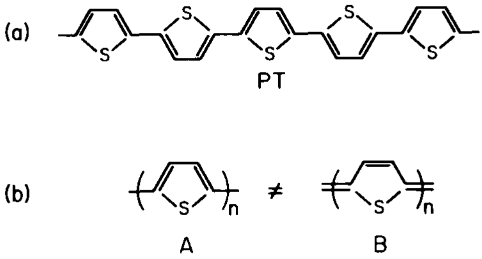
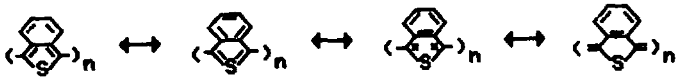


FIGURE 1 The two inequivalent structure of poly(thiophene). Where the energy content of A is lower than that of B.

As Bredas[1] has mentioned, this can be translated into a HOMO - LUMO gap difference between A and B. Alternatively, for poly(thiophene) "stabilization" of B (lowering the energy content) would make A and B almost isoenergetic, implying minimization of bond alternation and hence a decrease in Eg.

We reasoned that one way to accomplish this was to "lock" the 3,4 bond of thiophene as a double bond. The most obvious approach would be to make that bond part of an aromatic ring as in poly(isothianaphthene) (PITN, 1a - 1d, Figure 2); where



1a **1b** **1c** **1d**

x = +, −, •

FIGURE 2 Resonance contributors to the overall structure of PITN.

structure 1d would become an important contributor to the overall structure of PITN.[2]

RESULTS AND DISCUSSION

The monomer, isothianaphthene (ITN), had already been prepared by Cava sometime ago[3] in a straightforward way. In a recent publication we have described the conversion of this rather unstable monomer to PITN.[4] We have developed at least three different ways to produce the polymer; one of these is the highly desirable electrochemical film deposition on several different substrates such as conducting glass (ITO), platinum, etc. As formed, the film is blue and is *p* doped to an extent of ≃5% with chloride as counterion.

In Figure 3 we show that the blue films can be oxidized or reduced electrochemically (reversibly)[5] as determined by cyclic voltammetry. Armed with this information, it was straightforward to generate the electronic spectra shown in Figure 4 by *in-situ* doping a film of PITN generated electrochemically on

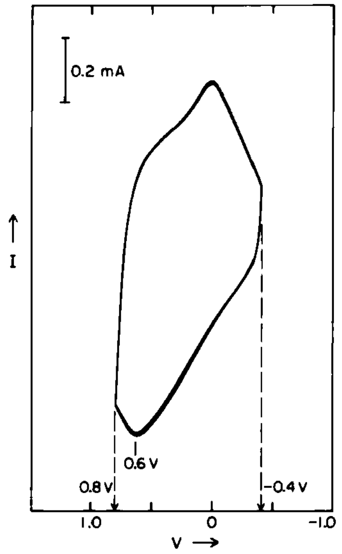


FIGURE 3 Cyclic voltammogram of PITN in propylene carbonate with $LiBF_4$ as supporting electrolyte, Al as counter electrode, and SCE as reference. The depicted curve corresponds to ≈60 cycles at a sweep rate of 10 mV per second.

ITO glass. The experimental details for the recording of these spectra were analogous to those used for similar spectroscopy on poly(thiophene).[6] This spectroscopy corroborated what had been observed visually; namely, that the film became greenish-yellow at the highest p doping level.[7] At heavily doped levels (applied voltage, 3.5V vs. Li), absorptions due to the interband transition have disappeared and the spectrum is qualitatively similar to that of a metal; i.e. all absorptions are in the infrared and appear to be due to free carrier absorption, very much as in the case of poly(thiophene).[6] Besides observing this unusual change with the naked eye, Masao Kobayashi also observed that the film became essentially transparent during the appropriate portion of the cyclic-voltammetry cycle.

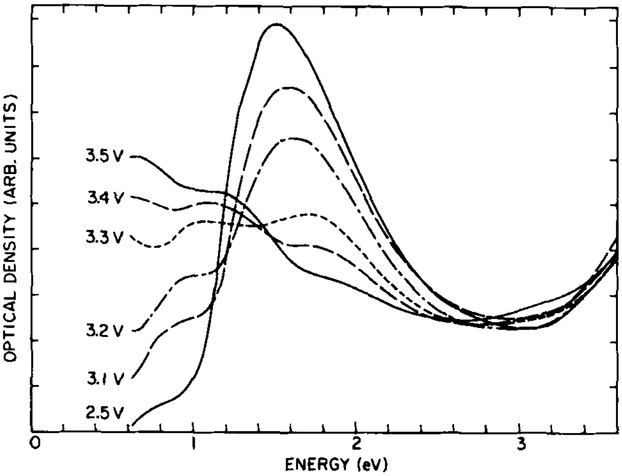


FIGURE 4 Electronic spectra of PITN film as a function of in-situ doping in THF with $LiBF_4$ as supporting electrolyte and Li as reference electrode.

Chemical doping of an electrochemically prepared film with iodine or Brønsted acids could be studied as a function of time. Figure 5 shows the result of such a study. In the same Figure it can be seen that the iodine doping can also be "compensated" with hydrazine vapor. For these experiments, PITN was grown on a microscope slide on which had previously been deposited four narrow strips ("fingers") of gold with ca 200μm separation between fingers; the growing polymer spanned the spaces between the gold. To perform conductivity measurements, the two outer fingers were connected to a dc current source and the inner ones to a voltmeter.

CONCLUSIONS

We have demonstrated that a polymer of isothianaphthene behaves in every respect like its relative, poly(thiophene); it can be produced electrochemically in film form and it can be reversibly

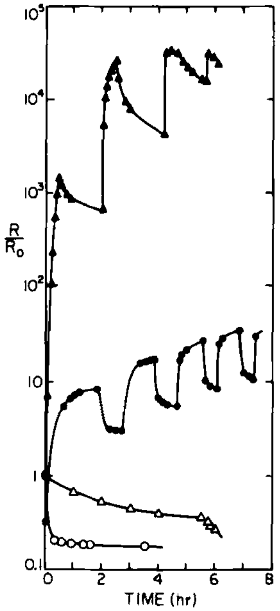


FIGURE 5 Resistance ratio during doping of PITN as a function of time. Open circles, iodine; open triangles, perchloric acid (vapor); closed circles, ammonia compensation; closed triangle, hydrazine compensation.

oxidized. It differs markedly from poly(thiophene) in that its bandgap appears at fully one eV lower in energy and that the electrochromic behavior is the reverse; i.e., p doping changes its color from blue-black to transparent, yellow-green.

REFERENCES

1. J.-L. Bredas, Mol. Cryst. Liq. Cryst., These Proceedings (1984).
2. There exists some controversy as to the weight of structures such as 1b relative to 1a in the case of the monomer. The relative importance of these structures in the case of the polymer is being ascertained by quantum chemical calculations by J.-L. Bredas.
3. M. P. Cava and A. A. Deana, J. Amer. Chem. Soc., 81, 4266

(1959). M. P. Cava, N. M. Pollack, O. A. Mamer, and M. J. Mitchell, J. Org. Chem., 36, 3932 (1971).

4. F. Wudl, M. Kobayashi, and A. J. Heeger, J. Org. Chem., 49, 0000 (1984).
5. Strictly speaking, electrochemical reversibility implies a theoretical peak-to-peak separation of ≃.06V. That is not observed in this case. What we mean by reversibility is that one can cycle this polymer at least over 60 cycles without noticeable change in the cyclic voltammogram (cf. Figure 3).
6. T.-C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev. B (July 1984).
7. Normally [e.g. poly(thiophene), poly(pyrrole)] it is the undoped state that has the lighter color [orange-red for poly(thiophene)] and the fully doped state exhibits the darker color [blue-black for poly(thiophene)].