Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoconduction in Conjugated Polymers

Michael Gailberger [a] , Binh Nguyen Thanh [a] & Heinz Bässler [a]

[a] Fachbereich Physikalische Chemie und Zentrum für Materialwissen-schaften der Philipps Universität., D-3550, Marburg, FRG

Version of record first published: 04 Oct 2006.

To cite this article: Michael Gailberger , Binh Nguyen Thanh & Heinz Bässler (1992): Photoconduction in Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 217-221

To link to this article: http://dx.doi.org/10.1080/10587259208046904

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 217–221
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Printed in the United States of America

PHOTOCONDUCTION IN CONJUGATED POLYMERS

MICHAEL GAILBERGER, BINH NGUYEN THANH, AND HEINZ BÄSSLER
Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften der Philipps Universität, D-3550 Marburg, FRG

Abstract Generation and transport of charge carriers in poly(phenylphenylenevinylene) and poly(3-dodecylthiophene) have been investigated by means of dc and transient photoconductivity. Geminate pairs are formed by disorder assisted partial dissociation of singlet excitons of chain segments followed by temperature and field assisted dissociation in accord with 1D Onsager theory. In PDT secondary hole injection from an AL-anode is responsible for quantum yields > 1. It is initiated by O_2^- ions accumulated at the interface.

INTRODUCTION

As far as their photo-electric properties are concerned conjugated polymers are usually considered to behave like semiconductors rather than like molecular crystals. The symbatic behavior between the action spectrum for light-induced charge carrier production and the occasional observation of a peak at the absorption edge[1] - often identified as the bandgap - is taken as evidence for a transition between π-type valence and conduction bands of the polymer. This contrasts with recent site-selective fluorescence studies on members of the poly(phenylenevinylene) (PPV) family[2] indicating that the absorption profile reflects an inhomogeneously broadened exciton transition coupling to vibrational modes of the chain. This conclusion will be supported by dc- and pulsed photoconductivity studies on poly(3-dodecylthiophene) (PDT) and poly(phenylphenylenevinylene) (PPPV).

EXPERIMENTAL

To minimize bimolecular recombination, notorious to occur under surface-electrode geometry[3], dc and pulsed photoconduction in PDT and PPPV was investigated in Al-contacted sandwich cells using a Xenon lamp and a N_2-laser as excitation sources, respectively. Time of flight studies were performed in conjunction with yield studies as a function of applied electric field, temperature and photon energy. Upon using a selenium layer as a hole injector TOF signals with well developed plateau regions were observed.

RESULTS

Fig. 1 shows a typical TOF trace for hole transport in PDT yielding mobilities that decrease with increasing electric field and saturate at $\simeq 5 \cdot 10^{-6}$ cm^2/Vs for $E \simeq 3 \cdot 10^4$ Vcm^{-1}. At higher fields the signals become progressively dispersive. Similar results are obtained with PPPV except that mobilities are about one order of magnitude higher.

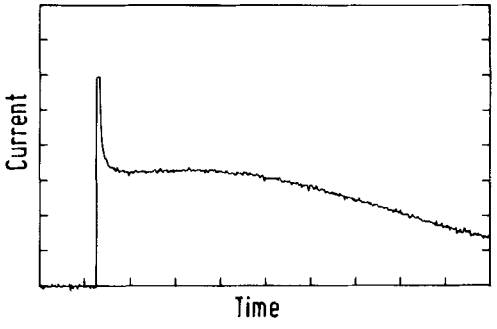
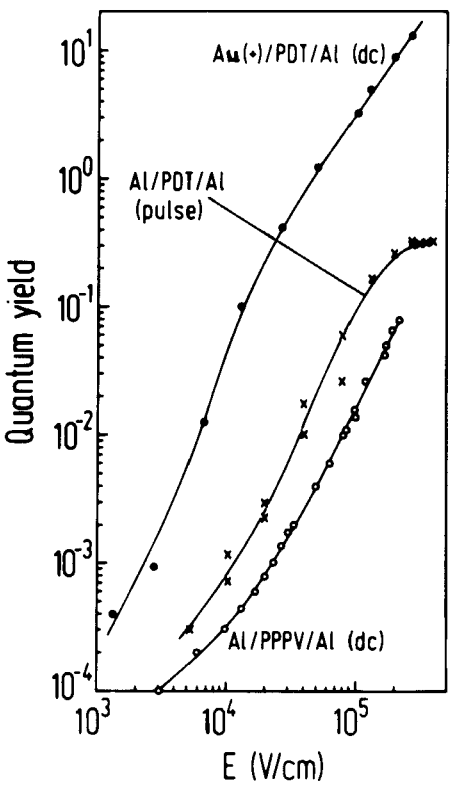


FIGURE 1 TOF signal for hole transport in PDT. (ordinate scale $5 \cdot 10^{-4}$ V/div, abscissa scale $2 \cdot 10^{-3}$ s/div, T = 293 K, E = $3.6 \cdot 10^4$ Vcm^{-1}, d = 11 μm)

Combined with the fact that dc and transient hole photocurrents are strictly linear in intensity observation of a transient signal documents that discharge at the contacts is the only loss mechanism for charge carriers. This guarantees that the quantum efficiency φ for charge carrier production can reliably be inferred from either dc-photocurrents or from $\int_0^\infty i(t)\,dt$ in the case of transient photocurrents. For both materials the number of charges produced per absorbed photon increases in proportion to the absorption coefficient at the absorption edge and exhibits some decrease - more pronounced in PPPV - above a photon energy corresponding to the peak of the inhomogeneously broadened $S_1 \leftarrow S_0$ 0-0 transition. In both cases φ is thermaly activated (E_a= 0.16 eV for PPPV and $\lesssim$ 0.1 eV for PDT) and strongly field dependent. In PDT yet not in PPPV dc-photocurrents as well as dark currents are oxygen sensitive. φ can reach values of order 10 if the sample is kept under ambient pressure (fig. 2).

FIGURE 2 Photocarrier quantum yield in PPPV and PDT. dc data for Au| PDT| Al were taken on a fresh sample under vacuum. After storing the sample at a pressure of 10^{-5}mbar for one week φ has decreased by about one order of magnitude.



DISCUSSION

$\varphi(h\nu)$ is interpreted in terms of disorder-enhanced dissociation of singlet excitons. The inhomogeneity of the $S_1 \leftarrow S_0$ transition is related to the variation of the effective conjugation length l_c of ordered segments along a polymer backbone, higher energies referring to shorter l_c. Upon scanning the excitation towards the band center the probability increases that a excitation can expand and form a coulombically bound e...h pair upon transfer of one of its constituent charges to an adjacent, more extended segment of the same or of neighboring chains. The expense in coulombic binding energy is compensated by the gain in site energy as illustrated in fig.3.

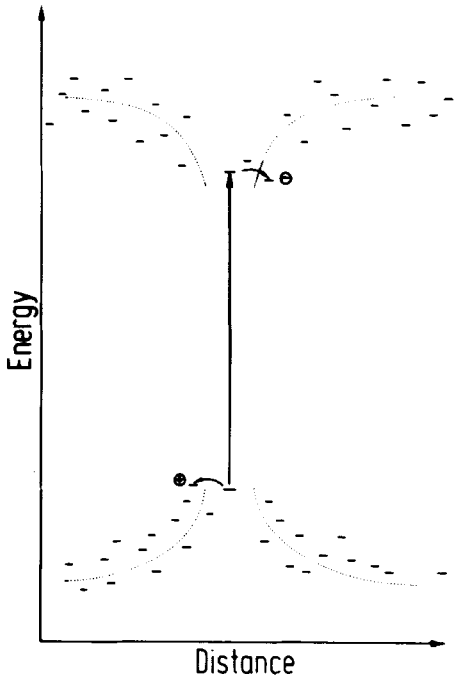


FIGURE 3 Illustration of disorder enhanced decay of a singlet exciton forming a geminate e...h pair

Subsequently the e...h pair can fully dissociate in course of an Onsager-like process, the field dependence being suggestive of 1 D behavior. The only

difference between the intrinsic photoelectric behavior of crystalline polydiacetylenes[4] (or other molecular crystals) and both PPPV and PDT is that disorder suppresses the threshold energy for e...h pair production thereby rendering singlet excitons capable of dissociating.

The oxygen effect observed with PDT is interpreted in terms of the migration of O_2^-, formed by capturing a primarily photogenerated electron by dissolved O_2, towards the AL anode. Once the potential established across an interfacial Al_2O_3 layer is large enough to match the difference between the Fermi level of Al and the top of the PDT valence band electrons can tunnel from PDT to the metal leaving holes behind on PDT chains, ready for transport across the sample.

Hole transport is controlled by hopping among segments of the polymer chains accidentaly differing in energy and mutual coupling. It is tractable in terms of the disorder formalism previously applied to analyse charge transport in molecularly doped polymers[5] and polysilanes[6].

Acknowledgement

BNT acknowledges a scholarship by DAAD.

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