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

# Role Of Geminate Recombination In Photovoltaic Spectral Responses Of Polyacetylene Junctions

F. Galluzzi [a] & M. Schwarz [a]
[a] Laboratori Assoreni, c.p.15, 00015 Monterotondo, (Rome), Italy
Version of record first published: 20 Apr 2011.

To cite this article: F. Galluzzi & M. Schwarz (1985): Role Of Geminate Recombination In Photovoltaic Spectral Responses Of Polyacetylene Junctions, Molecular Crystals and Liquid Crystals, 121:1-4, 301-304

To link to this article: http://dx.doi.org/10.1080/00268948508074879

*Mol. Cryst. Liq. Cryst.* 1985, Vol. 121, pp. 301-304
0026-8941/85/1214-0301/$10.00/0

Printed in the United States of America

# ROLE OF GEMINATE RECOMBINATION IN PHOTOVOLTAIC SPECTRAL RESPONSES OF POLYACETYLENE JUNCTIONS

F. GALLUZZI and M. SCHWARZ
Laboratori ASSORENI, c.p.15, 00015 Monterotondo (Rome) Italy.

Abstract Photoresponses of Schottky-type polyacetylene junctions are measured and compared with a theoretical model. Evidences for the importance of geminate recombination of photogenerated pairs are presented.

## INTRODUCTION

Photovoltaic properties of trans-polyacetylene (PA) have recently been the subject of many investigations[1] but several problems on the mechanisms of charge generation and transport still remain unsolved. In order to elucidate these aspects we undertaken an experimental study of spectral responses of Schottky and liquid PA junctions and elaborated a model able to describe experimental results.

## EXPERIMENTAL RESULTS

Solid-state metal-semiconductor junctions were prepared synthetizing Shirakawa-type PA films on aluminum coated (50-100 A thickness) glass substrates, while for liquid junctions Shirakawa-type free-standing PA films were used, dipped in de-oxygenated aqueous solutions with acetate buffer at pH 4-6.

Spectral responses of these junctions showed some dependence on sample morphology and history - in particular on polymer stretching - but essentially exhibited the same shape: the photoelectric signal is very small in the near infrared region (above 850 nm) and increases monotonously at shorter wavelengths up to 400 nm, showing no correlation with the absorption spectrum, peaked at about 600 nm.[1]

## A MODEL FOR SPECTRAL RESPONSE

In a semiconducting material the photocurrent quantum yield of a Schottky-like junction can be simply written[2]

$$\phi(\omega) = \int dx\, G(\omega, x)\, \eta_{gen}(\omega, x)\, \eta_{col}(x) \qquad (1)$$

where $G(\omega, x) = \alpha(\omega)\exp[-\alpha(\omega)x]$ is the e-h pairs photogeneration rate at the energy $\hbar\omega$; $\eta_{gen}(\omega, x)$ is the "free" carrier generation efficiency and $\eta_{col}(x)$ is the "free" carrier collection efficiency.

Only considering drift transport in the electric field region near the junction, the collection efficiency is

$$\eta_{col}(x) = \exp(-x/L_{dr}) \qquad (0 \leq x \leq W) \qquad (2)$$

where W is the depth of the field region and $L_{dr}$ is the drift length[2]. For the free carrier generation efficiency, on the other hand, we can neglect the dependence on position (x) and take into account two competitive processes: geminate recombination of photogenerated e-h pairs during relaxation, and e-h pair dissociation after relaxation. More precisely, we assume[3]

$$\eta_{gen} = K_{dis}/(K_{rec} + K_{dis}) \qquad (3)$$

where $K_{rec}$ is the probability per unit time of geminate recombination and

$$K_{dis} = K^{o}_{dis} \exp(- E_{dis}/KT) \tag{4}$$

is the probability per unit time of e-h dissociation, which follows an Arrhenius law with a dissociation energy barrier $E_{dis}$. At a first approximation, the dissociation barrier can be related to the relaxation time of excited e-h pairs $\tau_{rel}$ by an equation

$$E_{dis} \propto \tau_{rel}^{-\beta} \tag{5}$$

where $\beta$ is a proper exponent depending on the kind of relative motion of electron and hole (for instance $\beta = 1$ for classical drift motion and $\beta = 1/2$ for diffusion transport). On the other hand the relaxation time depends upon photon energy[3], being proportional to the excess kinetic energy of the photogenerated e-h pair.

For the dissociation probability we can write therefore:

$$K_{dis} = K^{o}_{dis} \exp\left[-Z(\omega-\omega_o)^{-\beta}\right] \tag{6}$$

where Z is a parameter and $\hbar\omega_o$ is a characteristic threshold related to the energy of relaxed dissociated pairs[3]. This approximate expression arises from a classical and oversimplified treatment of e-h dynamics and has to be considered therefore only a semiquantitative result, which, however, can be conveniently used for our purposes.

Inserting eqs. (2), (3), (6) in eq. (1) we obtain a simple explicit relationship for photocurrent quantum yield vs photon energy.

## COMPARISON WITH EXPERIMENTAL DATA

In order to elucidate the relative role of "free" carrier collection and "free" carrier generation in PA, we consider the theoretical model in two limiting cases.

Firstly, assuming a neglegible small geminate recombination rate and using PA absorption coefficients, we calculate spectral responses for $K_{rec}=0$ and for different values of $L_{dr}$. Resulting shapes reflect the absorption spectrum and do not show any agreement with experimental data.

Then we neglect losses in charge collection, assuming $L_{dr} \rightarrow \infty$, and consider spectral response shapes for a photogeneration-limited process. With this approximation, we observe a satisfactory agreement between our experimental data (between 400 and 800 nm) and the proposed model, obtaining reasonable values for free parameters ( $\beta = 1$, $\hbar\omega_o = .95$ eV, $K_{rec} > K_{dis}$ ) and confirming the importance of geminate recombination in PA.

## REFERENCES

1. M. Ozaki, D.L. Peebles, B.R. Weinberger, C.K. Chieng, S.C. Gau, A.J. Heeger and A.G. Mac Diarmid, Appl. Phys. Lett., 35, 83 (1979); B.R. Weinberger, S.C. Gau and Z. Kiss, Appl. Phys. Lett., 38, 555 (1981); J. Taukamoto, H. Ohigashi, K. Matsumura and A. Takehashi, Synt. Metals, 4, 187 (1982).
2. F. Galluzzi, J. Phys. D: Appl. Phys., 16, L261 (1983).
3. J.C. Knights and E.A. Davis, J. Phys. Chem. Solids, 35, 543 (1974); F. Galluzzi and M. Schwarz, Chem. Phys. Lett., 105, 95 (1984).