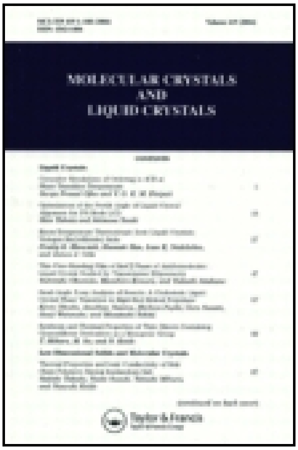

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Photoconductivity of Polyacetylene with Long and Short Light-Pulses

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PHOTOCONDUCTIVITY OF POLYACETYLENE WITH LONG AND SHORT LIGHT-PULSES

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Abstract For polyacetylene films, intrachain, interchain and interfibril effects can afford very different photoresponses in relation to the observed time scale. In the long time range (10^{-3}-10^{+2}s) the transient photocurrents are mostly related to trapping effects. Their analysis allows an estimation of the product $\mu\tau$ and the detrapping time constant ($\mu\tau = 3.10^{-11}$ cm^2/V and $\tau_p = 2.10^{-3}$s for a nearly cis sample). These photocurrents depend in a large amount on the cis/trans ratio.

INTRODUCTION

Trans-polyacetylene photoconductivity with fast excitation is the subject of numerous recent works, the aim of which is chiefly theoretical. In fact several processes can be effective in fast photoconductivity.[1-4] On the other hand, t-$(CH)_x$ is also a very studied material in view of practical applications and photoresponse in the "middle" or "slow" frequency range can be very important for the photovoltaic cells fabrication. These fast or slow time scales could correspond to very different transport phenomena: intrachain transport is available in the very fast range, but in the slow range, the interchain and interfiber phenomena could be preponderant. The characteristic transport parameters, as for instance the product $\mu\tau$, could then be different in these different time scales. However, experimentaly, this is not the case; with slow pulses, the obtained $\mu\tau$ values are not very different from those determined by fast measurements and the main factor controlling the transport in partly trans samples is the isomerization ratio, trapping steeply increasing with isomerization (i.e. with impurity content).

We then studied the trapping and detrapping in polyacetylene films with different cis/trans ratio by a detailed analysis of the transitory photocurrents described elsewhere.[5]

EXPERIMENTAL RESULTS AND INTERPRETATION

The transitory current shape is classical[6] especially with low isomerization (Fig. 1). A fast rise (AB), due to photo-carriers created by a band to band process is first seen. This rise is in direct ratio with the electric field and with the light flux. When the sample is mainly cis, only the UV light is efficient.The equilibrium among the conduction and valence bands is attained very rapidly with a time constant τ, corresponding to the lifetime of the photo-created minority carriers. When the light absorption coefficient is high the photocurrent can be given by

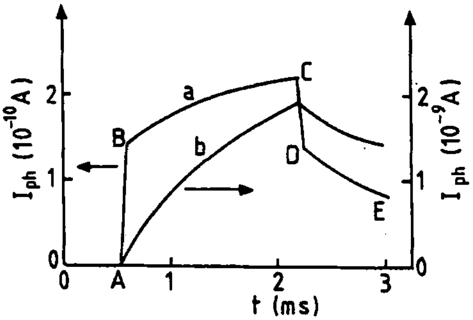

FIGURE 1 Transient photocurrent initiated with a light flash of length AC in cis (a) and trans(b) polyacetylene films.

$$\Delta i = 2\beta\tau I_0 e\mu EW\,(1-e^{-t/\tau}) \qquad (1)$$

where E is the electric field, I_0 the incident photon flux per cm^2, β the quantum yield of electron-hole pair per photon, W the length of the lightened electrode, μ the electron and hole mobility. τ has a too weak value to be directly measured but the product $\mu\tau$ can be calculated. For a mainly cis sample, $\mu\tau\sim3.10^{-11}cm^2/V$. This value must be compared with $\mu\tau=2.10^{-10}cm^2/V$ obtained on trans samples.[3]

The slower increase BC corresponds to the minority carriers entered into the sample to keep its electrical neutrality and, in this regime the photocurrent expressed by:

$$\Delta i = E\,\frac{W}{k}\,Ne\mu\,(1-e^{-t/\tau_p}) \qquad (2)$$

The trapping time τ_p is related to the trapping rate g, the light absorption coefficient k, the efficace electron capture cross section S, their velocity v and the empty traps density N:

$$\frac{1}{\tau_p} = g + 0.37\ \tau\beta kSvI_o \qquad (3)$$

The photocurrent saturation is nearly independent on the light flux and its value is $Ne\mu EW/k$. On the other hand the plot $1/\tau_p$ vs I_o can be used for an estimation of the trapping rate $g=5.10^2s^{-1}$.

When the light is off, the current decreases very steeply: CD is nearly equal to AB and is likely due to the excess carriers recombination in the valence and conduction bands. Then the detrapping of the trapped carriers is responsible of the slow variation observed after D. This scheme implies a recombination rate higher than the trapping rate and is more valid with mainly cis samples.

Although the red and infrared light begins to be efficient, the product $\mu\tau$ slowly increases from cis to trans samples. The $\mu\tau$ increase may be due to a very important mobility increase, even if τ decreases in agreement with the creation of soliton-antisoliton pairs[2] However this interpretation has been questionned by Yacoby et al.[7] from flight time experiments on pure trans-$(CH)_x$ samples. Using their value of τ and our value of the product $\mu\tau$, a mobility of about $10^2cm^2/V$ is estimated. It would then appear that, although obtained with long pulses, such a value is characteristic of a "chain" mobility.

In fact the behavior of trans-polyacetylene is more complex; the purity of the samples is an important parameter: a high purity decreases by orders of magnitude the dark conductivity and the photoconductivity.[8] Several machanisms corresponding to the various parts of the excitation spectrum have been pointed out. In the studied wavalength range, the hopping of the carriers may play an important role as soon as the sample is a little isomerized: there are trapping and detrapping of the carriers, each carrier being trapped and release many times. This hopping could be efficient in all the samples in particular when the conductivity becomes to be one-dimentional. It would then be less surprising that the μ value obtained in the slow time scale is not very different from its value determined by very fast technics.

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