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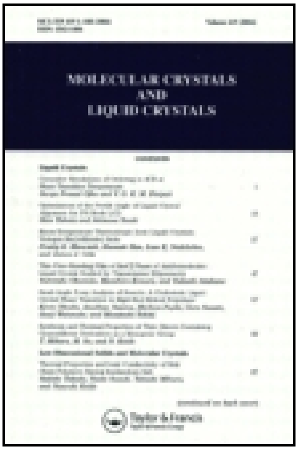

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Transient Photocurrents in Amorphous and Polycrystalline 1,5-Diphenyl-3βStyrylpyrazoline (DSTP)

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TRANSIENT PHOTOCURRENTS IN AMORPHOUS AND POLYCRYSTALLINE 1,5-DIPHENYL-3ßSTYRYLPYRAZOLINE (DSTP)

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Abstract Charge transport properties of a pyrazoline derivative both in its polycrystalline and amorphous solid state are measured and discussed.

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INTRODUCTION

The charge carrier transport properties of organic solids are determined by means of transient photocurrent measurements[1,2]. This technique, commonly used for single crystals or amorphous samples, is seldom applied to vapor deposited organic polycrystalline films[3-11] in spite of their potential technological use in photovoltaic devices or in electrophotography, probably due to some difficulties in the experiment and in the interpretation of its results.

One such interesting material is DSTP (Figure 1), a pyrazoline derivative.

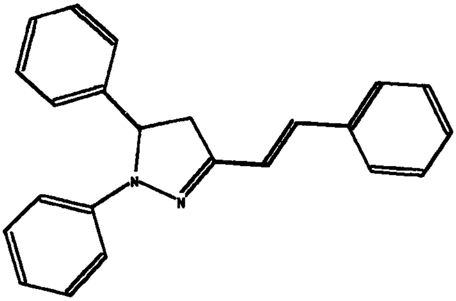

FIGURE 1 1,5-diphenyl-3ßstirylpyrazoline (DSTP)

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It is known that pyrazolines are a class of compounds showing good photoconductive properties and forming stable amorphous or polycrystalline films at room temperature[12-15]. With regard to DSTP, its effectiveness as charge transport layer (CTL) in layered photoconductor systems for electrophotography has been studied only as a dopant dissolved in a polymer matrix[12,15]. In a matrix containing 50% of DSTP and 50% of the polymer, the hole mobility was found to be about $2x10^{-7}$ cm^2/Vs at a field of $2x10^5$ V/cm.

In this paper we report, for the first time, the mobility of a pyrazoline derivative both in the amorphous and in the polycrystalline phase. At about the same applied field ($1.2x10^5$ V/cm) the crystalline film shows a room temperature hole mobility of $1.8x10^{-5}$ cm^2/Vs. The hole mobility in the amorphous film is one order of magnitude lower.

An interesting feature of polycrystalline DSTP is the lack of the anomalous drift mobility behaviour often observed in other polycrystalline materials[3,16-22]. Besides, our results show, for the first time, an example of a crystalline organic film having a strong temperature and electric field dependence of the mobility.

EXPERIMENTAL

DSTP was purified by chromatography and sublimation. Thin transparent amorphous films were easily obtained by vapour deposition at a controlled rate onto a quartz substrate, at a pressure of 10^{-4} Pa. After few hours at room temperature, however, the amorphous films change into a partially crystalline phase. Full transformation was achieved by heating the samples for one day at 70 °C. Stable amorphous films suitable for prolonged electrical measurements were obtained by melting the DSTP between two semitransparent electrodes and then rapidly quenching the melt.

The transient photoconductivity measurements were performed on the following sandwich cell arrangement: semitransparent Al electrode deposited onto a quartz plate / 8-40 µm polycrystalline or amorphous DSTP / 1 to 4 semitransparent top Al electrodes evaporated onto the film (electrode area = 0.78 - 0.06 cm^2). Contacts to Al electrodes were made using aquadag. The sample, during the measurements, was mounted in a variable-temperature evacuable chamber.

As the light source, a pulsed nitrogen laser was used having an

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average maximum energy of 3 mJ/pulse at 337 nm and a pulse duration of 8 ns. The laser energy was measured by means of a Laser Precision power meter.

The transient photocurrents were detected and analysed by means of a Tektronix 468 oscilloscope interfaced with an Apple II E computer.

The laser energy impinging on the front electrode was lower than 0.1 mJ/cm^2 in order to aviod the influence of space charge.

The optical density of DSTP was high enough to ensure surface excitation followed by a surface photogeneration process.

RESULTS AND DISCUSSION

The shapes of the signals obtained from polycrystalline DSTP samples were strongly dispersive over the entire temperature and electric field ranges investigated, thus preventing a direct acquisition of the transport parameters (Figure 2a). By replotting the signal on a double logarithmic scale (Figure 2b), it was possible to obtain the transit time and consequently the effective mobility of the majority carriers (holes).

Following the theoretical models for dispersive transport[23], the form of the photocurrent I(t) is:

$$I(t) \propto t^{-(1-\alpha_i)} \qquad \text{for } t \le t_T$$

$$I(t) \propto t^{-(1+\alpha_f)} \qquad \text{for } t \ge t_T$$

were α_i and α_f are coefficients <1 and >0.

The hole transit time t_T is indicated on the time scale by the slope change from $-(1-\alpha_i)$ to $-(1+\alpha_f)$.

In order to have a large enough time range for a better determination of α_i, α_f and t_T, the curve in Figure 2b was obtained by superimposing in the log-log scale subsequent single transient photocurrent signals in the same experimental conditions, just changing the time and voltage scales and the input resistance on the oscilloscope.

In the case of the amorphous samples, the transport properties were investigated only near room temperature in order to avoid any crystallisation onset. The signals obtained were strongly dispersive. At a field of about 2.7x10^5 V/cm, however, they were characterized by the appearance of a plateau followed by a dispersive tail (Figure 3a,b), thus allowing a direct determination of the transit time.

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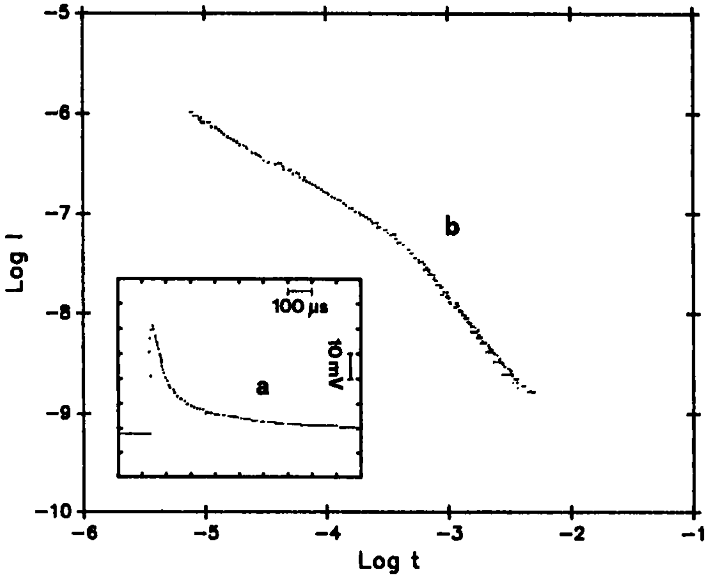

FIGURE 2 Tof signals for polycryst. DSTP at room temperature and 100 V applied voltage. Sample thickness is 8.5 µm.
(a) typical signal shape (V(t) vs t)
(b) photocurrent vs time in double logarithmic scale.

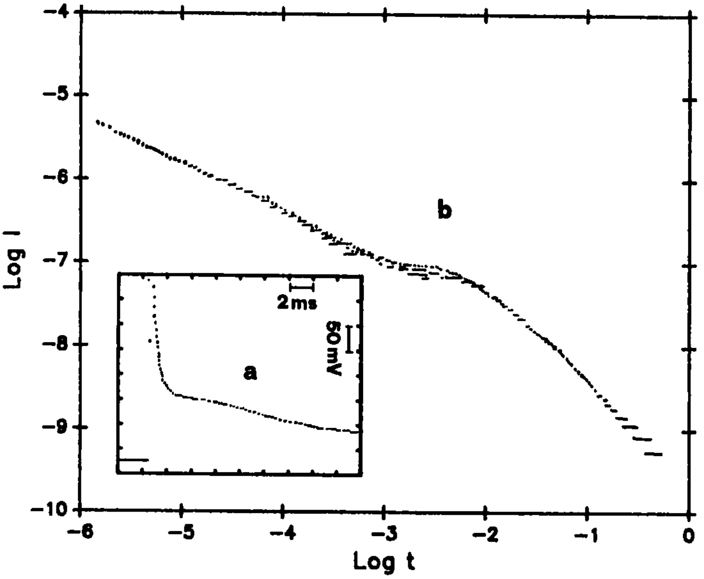

FIGURE 3 Tof signals for amorphous DSTP at room temperature and 1000 V applied voltage. Sample thickness is 40 µm.
(a) typical signal shape (V(t) vs t)
(b) photocurrent vs time in double logarithmic scale.

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In Table I and in Figures 4 and 5 some preliminary results are reported. They can be summarized as follows:

1) The transport is dispersive both in polycrystalline and amorphous DSTP. However, the transient signals don't exibit the Scher-Montroll 'universality' of current vs time dependence. In fact $\alpha_i \neq \alpha_f$ and, in polycrystalline DSTP, both change with the temperature. Dispersive transport has been observed in amorphous or disordered films and various models have been proposed in order to explain this behaviour[23]: (a) a pure dispersive hopping, (b) trap-controlled hopping or (c) multiple trapping.

TABLE I Tof data for polycrystalline DSTP. Transit times (t_T) obtained from the plots Log I vs Log t; $\mu = l^2/V_{app} * t_T$, l(thickness)=8.5 μm.

Temp [K]	V_{app}	t_T [sec]	slope $t<t_T$	slope $t>t_T$	μ [$cm^2/Vsec$]
295	40	$4.80\ 10^{-3}$	-0.82	-1.27	$3.76\ 10^{-6}$
	60	$2.40\ 10^{-3}$	-0.71	-1.38	$5.01\ 10^{-6}$
	80	$1.10\ 10^{-3}$	-0.69	-1.43	$8.21\ 10^{-6}$
	100	$4.08\ 10^{-4}$	-0.71	-1.59	$1.77\ 10^{-5}$
308	40	$4.13\ 10^{-3}$	-0.57	-1.41	$4.37\ 10^{-6}$
	60	$1.10\ 10^{-3}$	-0.53	-1.40	$1.09\ 10^{-5}$
	80	$3.86\ 10^{-4}$	-0.58	-1.40	$2.34\ 10^{-5}$
	100	$1.77\ 10^{-4}$	-0.55	-1.42	$4.08\ 10^{-5}$
322	40	$1.01\ 10^{-3}$	-0.55	-1.24	$1.78\ 10^{-5}$
	60	$5.52\ 10^{-4}$	-0.55	-1.44	$2.18\ 10^{-5}$
	80	$2.62\ 10^{-4}$	-0.54	-1.53	$3.44\ 10^{-5}$
	100	$1.28\ 10^{-4}$	-0.49	-1.50	$5.64\ 10^{-5}$
343	40	$6.55\ 10^{-4}$	-0.54	-1.31	$2.75\ 10^{-5}$
	60	$2.08\ 10^{-4}$	-0.54	-1.22	$5.78\ 10^{-5}$
	80	$9.51\ 10^{-5}$	-0.46	-1.19	$9.49\ 10^{-5}$
	100	$5.76\ 10^{-5}$	-0.47	-1.23	$1.25\ 10^{-4}$

For amorphous DSTP the choice should be restricted to the last two models. In polycrystalline DSTP the transport should be uniquely controlled by multiple trapping and thermal detrapping processes.

2) In polycrystalline DSTP holes are the majority carriers and the room temperature value of hole mobility is 1.8×10^{-5} cm^2/Vs, at 1.2×10^5 V/cm. This value, although low if compared with other polycrystalline organics[3-11], is about one order of magnitude higher with

respect to amorphous DSTP, which shows a hole mobility of 2.7×10^{-6} cm^2/Vs at 2.7×10^{5} V/cm. Finally, the same material dissolved in a polymer matrix (50% DSTP, 50% polymer), at a field of 1.25×10^{5} V/cm, has a hole mobility of 2×10^{-7} cm^2/Vs[15], i.e. two ordersof magnitude lower compared to the polycrystalline counterpart.

3) Polycrystalline organic compounds generally show a constant or a decreasing value of the mobility when the applied field increases (anomalous drift mobility)[3,16-22]. Furthermore, mobility activation energies, apart from one case[11], have been found to be ≤ 0.11 eV. The polycrystalline DSTP behaviour is an interesting exception to this general trend. No anomalous drift mobility was in fact observed in this material (Figure 5 indicates that mobility increases with the electric field). Moreover mobility is temperature activated with an activation energy between 0.44 and 0.34 eV, depending on the applied electric field (Figure 4).

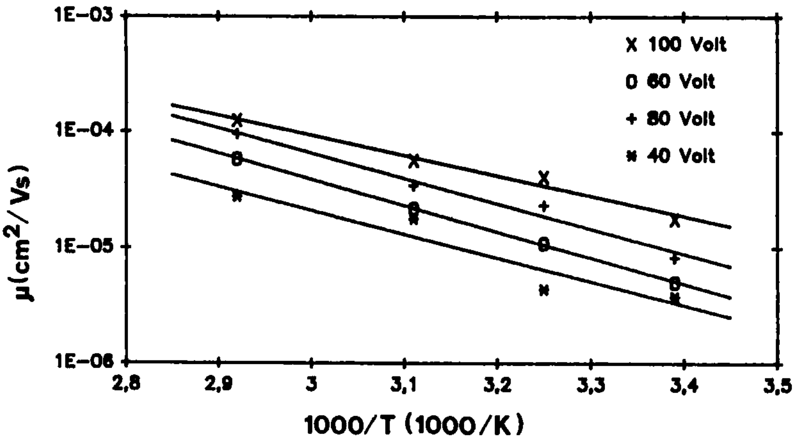

FIGURE 4 Temperature dependence of hole mobility in polycrystalline DSTP.
Parameter is the applied voltage
(sample thickness is 8.5 μm)

A similar electric field dependence of the mobility has been often observed in amorphous solids and has been explained as due to a Poole-Frenkel effect.

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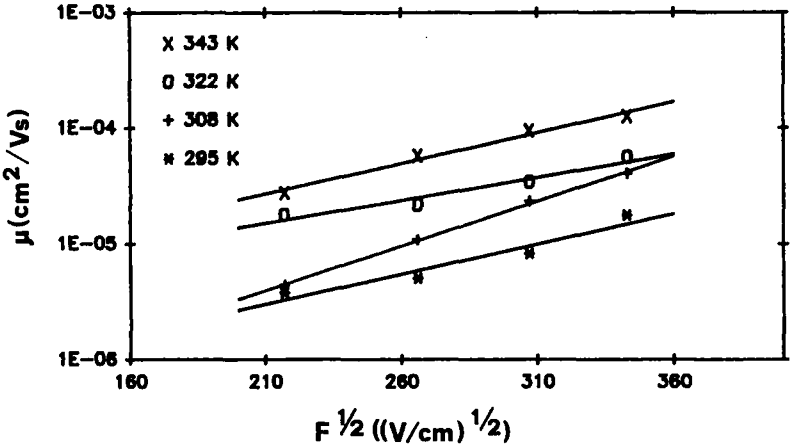

FIGURE 5 Electric field dependence of hole mobility in polycrystalline DSTP.
Parameter is the temperature.

The Poole-Frenkel model, however, requires the presence of a high density of charged coulombic centers and this is in contrast with the neutral nature of DSTP. In order to explain this behaviour, new models concerning charge traps should be tested.

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