

SHORT COMMUNICATION

Trap-Free Drift Mobility in Poly(*N*-vinylcarbazole)

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An attempt was made to estimate the trap-free drift mobility in poly(*N*-vinylcarbazole) (PVCz) directly from the current value in transient photocurrent curves. A value of about $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained. Also, it was found that the initial spike-like transient photocurrent observed in PVCz is mainly due to the transient trapping process of the carriers produced initially by the irradiation of light pulse.

The carrier transport in amorphous photoconducting polymers, *e.g.*, PVCz, is considered to be a thermally activated hopping conduction from trap to trap. In agreement with this, very low drift mobilities of the order of $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported.²⁻⁴ A number of attempts have been made to account for the transient photocurrent in low-mobility materials.⁵⁻⁹ Scher and Montroll⁵ introduced the concept of the time distribution of hopping events to explain the pulse shape of photocurrent, while Marshall and Owen⁶ showed by computer simulation a thermally activated hopping model to be also valid as an alternative interpretation for the transient photocurrent pulse. Recently, Demura *et al.*⁹ attempted an analysis of the transient photocurrent shape by computer simulation and a trap-limited model. The present analysis was thus made on a thermally activated hopping model involving the concept of trap-free drift mobility.

In this model for carrier transport, the transient photocurrent at a given time *t* in a time-of-flight measurement can be written, assuming a single discrete trapping level to be operative as the first approximation, as follows:

$$I_{\text{obs}} = \frac{1}{d} \cdot e \cdot \mu_f \cdot F \cdot n_0 \times \left[\frac{\tau_t}{\tau_f + \tau_t} \cdot \exp \left\{ - \left(\frac{1}{\tau_f} + \frac{1}{\tau_t} \right) t \right\} + \frac{\tau_f}{\tau_f + \tau_t} \right] \quad (1)$$

where τ_f is the lifetime of free carriers, τ_t the lifetime of trapped carriers, *d* the sample thickness, *e* the electronic charge, μ_f the trap-free drift mobility, *F* the applied electric field, and n_0 the number of total carriers.

The first exponential term in the brackets in eq 1 represents the transient process to a quasi-steady state of trapping and detrapping processes, and is dominant at small *t*. The second term shows the ratio of free carriers to the total carriers which is assumed to be in trapping-detrapping thermal equilibrium, and indicates that only free carriers contribute to the photocurrent at any given time. Since τ_t is much larger than τ_f , as is assumed generally, meaning that the number of trapped carriers, n_t , is much larger than that of free carriers, n_f , one may introduce the following relation into this ratio:

$$\begin{aligned} \tau_f / (\tau_f + \tau_t) &\simeq n_f / n_t \\ &= \exp(-E_a / 2kT) \end{aligned} \quad (2)$$

where E_a is the activation energy for the trap depth. The coefficient 2 preceding *kT* is introduced in order to take the Fermi-Dirac distribution of trapped and detrapped carriers at thermal equilibrium into account.¹⁰

The first term in eq 1 is negligible at sufficiently large time, at which the transient photocurrent curve gives an apparent plateau. Hence, I_{obs} can be

Table I. Calculation of trap-free drift mobility μ_f

Field, F	Obsd current, ^a $i_{d/2}$	Total carrier, ^b n_0	Free carrier, ^c n_f	Drift mobility, ^d μ_f
$V\text{ cm}^{-1}$	amp			$\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$
3.15×10^5	9.08×10^{-9}	6.68×10^9	1.89×10^5	5.72×10^{-4}
3.93	2.40×10^{-8}	1.11×10^{10}	4.45	5.15
4.72	4.96	1.62	9.05	4.35
5.50	1.09×10^{-7}	2.17	1.63×10^6	4.56
6.30	2.29	2.92	2.90	4.70

^a Observed photocurrent value at $t = t_t/2$.

^b Obtained from the integration of transient photocurrent.

^c Calculated using eq 2 and 4 in the text; $E_0 = 0.68\text{ eV}$,² $\beta = 2.72 \times 10^{-4}\text{ eV}/\sqrt{V/\text{cm}}$,² $T = 292\text{ K}$.

^d Calculated from eq 3 in the text.

reduced to,

$$I_{\text{obs}} = (1/d) \cdot e \cdot \mu_f \cdot F \cdot n_0 \cdot \exp(-E_a/2kT) \quad (3)$$

Here, the number of total carriers, n_0 , can be obtained from the integration of transient photocurrent. Other variables are also obtainable under the experimental conditions. Thus, the trap-free drift mobility μ_f can be estimated.

Measurements of transient photocurrent were made in a sandwich-type cell having a (Au/PVCz/nesa) construction by irradiating incident light pulse (N_2 gas laser, 337 nm, pulse width 3 ns) on the positively biased nesa electrode.

Table I lists μ_f values at various fields obtained by analyzing the observed data according to eq 3. In the calculations, it was assumed that at $t = t_t/2$ (t_t : transit time), at which most of the carriers have passed the halfway distance of the sample, thermal equilibrium of carriers is attained. The current value $I_{d/2}$ at $t = t_t/2$ was used. For the trap depth, E_0 , a value of 0.68 eV was used as reported by Gill² for PVCz. In evaluating E_a , the Poole-Frenkel type of barrier lowering was taken into account, *i.e.*,

$$E_a = E_0 - \beta\sqrt{F} \quad (4)$$

It is seen that the values of μ_f obtained are almost constant for various fields, being about $5 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. This value is about 10^4 times larger than the overall drift mobility of *ca.* $10^{-7}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, and reasonably compares with those reported by Reimer *et al.*¹¹ and Hirsh,¹² who also attempted to estimate μ_f by different experiment.

Figure 1 shows a rough sketch of the transient photocurrent profiles based on the idea that μ_f is

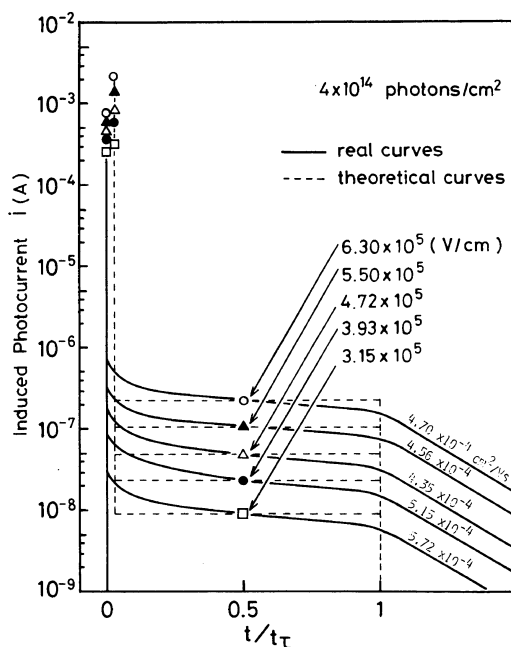


Figure 1. Field dependence of transient photocurrents in PVCz. The solid and broken curves represent the observed and theoretical curves, respectively. Applied fields, as indicated; time axis is normalized by transit time, t_t ; sample thickness, $6\text{ }\mu\text{m}$; measured at 292 K *in vacuo*.

independent of the field strength. As the field increases, $I_{d/2}$ increases. This can be considered due to an increase in free carrier density n_f arising from an increase in total carrier (n_0) yield and the Poole-Frenkel barrier lowering under applied fields, but not due to the field-dependence of drift mobility

itself. In the initial non-equilibrium state, only the first term in eq 1 is operative, and, therefore, all the photocarriers produced can move toward the counter electrode. The initial peak current values evaluated using a constant μ_t and respective n_0 values at various fields show good agreement with the experimental data, as shown in Figure 1. This indicates that a large current drop subsequent to the initial photocurrent peak is caused mainly by transient trapping before the thermal equilibrium state of trapped and detrapped carriers is attained. A detailed analysis of the initial peak current will be presented in a forthcoming paper.

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