Hole Transport in Polyvinylcarbazole: The Vital Importance of Excitation-Light Intensity

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Transient photoconductivity measurements of holes in polyvinylcarbazole are reported. It is found that good agreement with the dispersive transport theory of Scher and Montroll is obtained only for light intensities two orders of magnitude below values conventionally used. In contrast to earlier results, we find a single temperature-independent value of α equal to 0.66 ($\pm$ 0.05).

In recent years there has been considerable interest in the dynamics of charge carriers and energy diffusion in disordered systems. This interest has been stimulated in part by the importance of amorphous materials as photo-conductors[1] and semiconductors[2] and in part by the development of increasingly sophisticated theories to handle spatial and energy disorder.[3-6]

Much of the experimental work has concentrated on a comparison of experimental data with the continuous-time random-walk theoretical approach of Scher and Montroll.[7] For some systems, like As$_2$Se$_3$,[8] there seems to be excellent agreement in all respects with the theory. For other systems, such as hole transport in the polymer polyvinylcarbazole (PVK), discussed here, previous results were inconsistent with the theory in certain important respects.[9,10] *It will be the essential conclusion of this paper that if one works at low enough light intensities to avoid interaction between optically created charge carriers, one finds excellent agreement with theory in the case of PVK.*

The time-of-flight (TOF) technique[11-13] has been the primary tool for the study of photoconductivity in single crystals[14] and amorphous systems.[1] In this type of experiment a sheet of charge is created by a pulse of light at one electrode. The sheet then moves through the sample to the other electrode under the influence of the applied electric field. One measures the current so produced as a function of time. This process is governed by a hopping rate W with the following functional form:

$$W \propto e^{-r/r_0} e^{-\Delta E/kT} \tag{1}$$

where r is the distance between hopping sites, r_0 characterizes the range of the interaction responsible for hopping and ΔE the energy difference between sites; k and T are Boltzmann's constant and the temperature, respectively. In an ordered single crystal, W is a constant and the hopping-time distribution is exponential:

$$\Psi(t) \propto e^{-Wt}. \tag{2}$$

Ordered systems thus exhibit Gaussian transport because of the Gaussian nature of the wave packet moving through the material. Scher and Montroll recognized that in a disordered system there is a wide distribution of W's leading to a range of hopping times extending well into the experimental time scale. In this case one can express the extent of the disorder by the parameter α, defined by the equation

$$\Psi(t) \propto t^{-(1+\alpha)}, \tag{3}$$

where α ranges between 0 and 1; the smaller α the greater the disorder. This type of transport is called dispersive transport.

For a TOF experimental Scher and Montroll predicted that the shape of the current transients can be described by two distinct algebraic time dependencies. Initially, the current transient is given by

$$I(t) \propto t^{-(1-\alpha)}. \tag{4}$$

After some of the carriers have had a chance to leave the sample [$t > t_{tr}$, where t_{tr} is the transit time defined in Fig. 1(a)], the current behavior becomes

$$I(t) \propto t^{-(1+\alpha)}. \tag{5}$$

Equations (4) and (5) imply that a single α should be sufficient to describe the entire transient. The theory also predicts that a universal master plot can be created if both the current and the time are normalized with respect to t_{tr}. This universal plot should be obtained regardless of the externally applied voltage.[7,8,15]

In this publication we report TOF measurements for hole transport in PVK clearly demonstrating that dispersive transport describes this material with a single value for α, in contrast to earlier experiments that require a different α for the two parts of the transient.[9,10] Furthermore the α value that we obtain is independent of temperature, again in contrast to the temperature-dependent value found earlier.[9,10] The origin of the difference between the present results and earlier experiments lies in the light intensity used to obtain the transients. We have found that even in the small-signal limit, when the number of charge carriers created (measured by integration of the transient current pulse) is less than the stored charge on the electrodes ($Q < CV$), the α's derived depend substantially on the excitation inten-
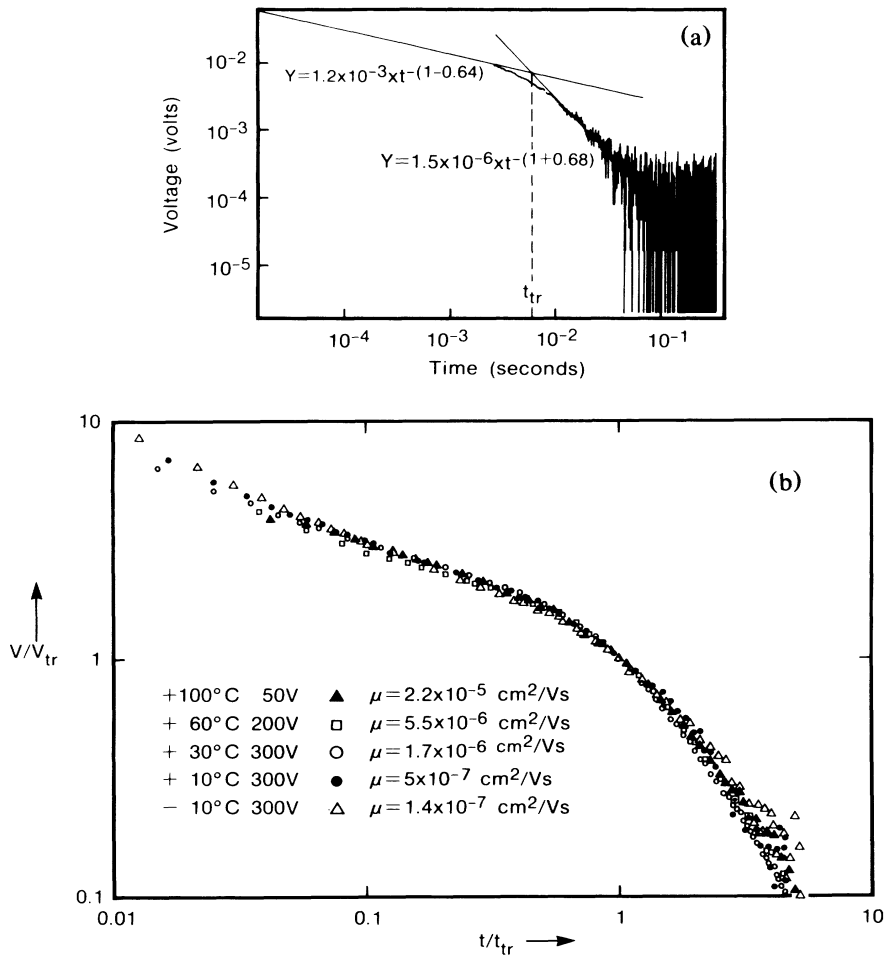
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FIG. 1. (a) Typical time-of-flight transient plotted on a log-log scale. The algebraic time dependences as derived from a least-squares-fitting routine are also shown. The dashed line indicates the transit time. To derive the actual voltages the readings along the ordinate should be divided by 20 to compensate for the preamplifier D1000 amplification. (b) Universal master plot of transients obtained at several temperatures and voltages. The mobilities (μ) given in the figure are derived from $\mu = L^2/Vt_{tr}$. $L = 10$ μm (sample thickness); V is the applied voltage and t_{tr} is the transit time defined in (a).

sity used. Only when we reduced the light intensity to a value three orders of magnitude below the stored charge were we able to obtain an intensity-independent α. At this intensity the number of charge carriers generated is typically $10^{10}/\text{cm}^2$.

Several experimental details permitted us to work at these low light intensities. The data were recorded with the use of a digital wave-form analyzer and fed directly to a computer for storage, analysis, and display. This arrangement allows a horizontal and vertical dynamic range of over four orders of magnitude to be recorded in a single shot with a sensitivity of less than 1 μV. In addition, by using the pretriggering capabilities of the wave-form analyzer, we obtained the accurate baseline necessary for proper analysis of the data on log-log plots.

Also important for reliable and reproducible transient

shapes is to make sure that few trapped charges remain in the sample from previous shots. We found that the best way to accomplish this was to allow the sample to relax for 45 min or more in the dark with the voltage still across the sample. Our sample preparation was similar to methods described in the literature.[9,10,16] The holes were generated by exposure of the PVK through the Mylar to a 10-ns pulse of typically 5 μJ from a N_2 laser. The rear electrode was formed with use of Ag epoxy.

Figure 1(b) shows a plot of the normalized experimentally observed transients for holes in PVK for several voltages and at several temperatures. Each point is the average of four consecutive measurements. As expected universality is observed, not only for measurements at various voltages, but also for measurements made at different temperatures. In Fig. 2, we compare the α's
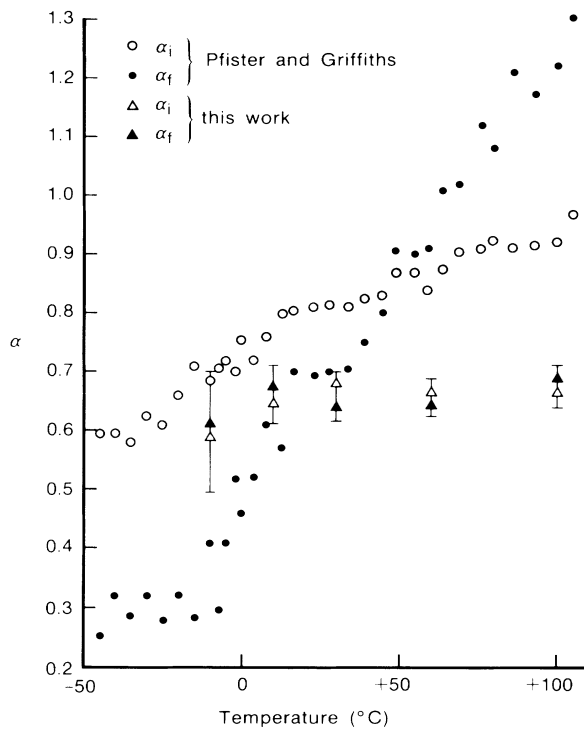
FIG. 2. Comparison of the α's taken from Ref. 9 with the α's obtained in this study.
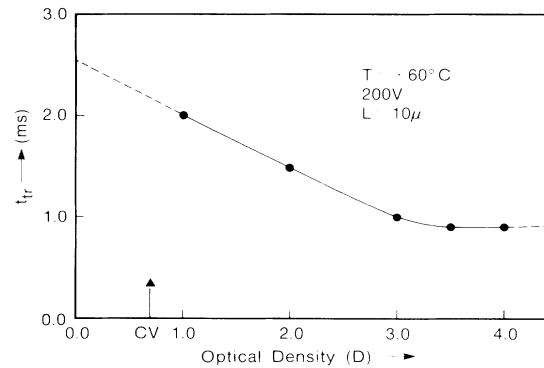

FIG. 3. The transit time derived from a log-log plot as a function of excitation light intensity. $D = 0$ corresponds to 5 mJ. The arrow indicates the stored charge (CV) for this experiment. The transit time reported in Ref. 9 was 4 ms under comparable circumstances.

determined from our measurements with the earlier work of Pfister and Griffiths.[9] In the earlier work it was necessary to define two α's: α_i for times shorter than t_{tr} and α_f for times longer than t_{tr}. Our results clearly indicate that a single temperature-independent value of $\alpha = 0.66 \pm 0.05$ describes the experimental transients.

Conventional space-charge effects, resulting in a nonhomogeneous field E across the sample, require one to work with charge concentrations below 10% of CV.[17] Our results, which indicate that it is necessary in a typical configuration to reduce the concentration to values below 0.1%, clearly cannot be explained by space charge in this conventional sense. Our current view is that the laser-intensity–induced distortion of the current transient is due to lateral Coulomb spreading of the initially generated packet of charge. A numerical calculation of the Coulomb force perpendicular to the externally applied electric field shows that for a typical case the field is reduced to a negligible 10% of the force due to the external field only when the charge concentration is reduced to 0.1% of CV. In a perfect crystal or gas this lateral Coulomb spreading would cause a broadening of the ensemble of charge carriers but would not substantially affect the shape of the transient curve. In a disordered medium, however, the carrier transit time is not linearly dependent on path length.[7] The different paths

(and path lengths!) traversed by the charged particles can be described by effectively different time-dependent mobilities leading to a distortion of the current transient shape.

Figure 3 shows measurements of the transit time as a function of light intensity. Clearly the measured transit time is also sensitive to the number of holes generated in the sample. Our experimental measurements approach those of Pfister and Griffiths[9] at higher light intensities. Measurements of t_{tr} (or mobility) made at high light intensities must thus be viewed with caution. Perhaps some of the inconsistencies in the functional form of mobility versus electric field and temperature may be due to this effect.[18]

Finally some remarks on the temperature independence of α are in order. The value is determined by an ensemble of transition rates given by Eq. (1). A temperature-independent α means that the Boltzmann distribution of energy levels is not important. The dynamics of the continuous-time random walk is determined only by the geometry of the amorphous system. Blumen et al.[19] have shown that α can be divided into two contributing factors, γ due to fluctuations in hopping times and β reflecting the geometry of the lattice:

$$\alpha(T) = \gamma(T)\beta. \tag{6}$$

$\gamma(T)$ is related to Eq. (1) and has the same physical origin as the conventional dispersion parameter α described by Scher and Montroll. The fact that $\alpha(T)$ in Eq. (6) does not depend on temperature means that γ, like β, depends on geometry alone. β is given by

$$\beta = \tilde{d}/\bar{d}, \tag{7}$$

where $\tilde{d}$ is the spectral dimension and $\bar{d}$ is the fractal dimension.[6] If the underlying geometry of the amorphous PVK can be described as a Euclidean space, then $\beta = 1$

and $\gamma = 0.66$. If the amorphous polymer is described by a fractal dimension and, furthermore, if we use the Alexander-Orbach conjecture that relates spectral and fractal dimensions,[20] we obtain the relation

$$\gamma/\bar{d} = \tfrac{1}{2}.$$

Experiments are now under way to determine more precisely the geometry of the hole transport in PVK by determining an empirical value for $\bar{d}$.

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