PHYSICAL REVIEW B VOLUME 39, NUMBER 17 15 JUNE 1989-I

Dispersive nature of hole transport in polyvinylcarbazole

F. C. Bos,* T. Guion, and D. M. Burland
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

(Received 25 October 1988; revised manuscript received 15 December 1988)

Hole transport in polyvinylcarbazole (PVK) is investigated, with a particular emphasis on comparing the experimental results with the theoretical predictions of the continuous-time random walk (CTRW) model. It is found that hole transport in this system exhibits all of the characteristic features of the CTRW model including universality, the predicted functional form of the time-of-flight transient, and the appropriate thickness dependence of the transit time. The electrical field dependence of the transit time has also been investigated. It is not possible to distinguish which of the various field-dependence models describes hole transport in PVK. In particular, both the Poole-Frenkel and kinetic models of the hopping process fit the data with physically reasonable parameters.

I. INTRODUCTION

Charge-carrier and energy transport in amorphous systems have been the subject of much experimental and theoretical interest in recent years. A variety of systems has been investigated experimentally: pure polymers,[1] molecularly doped polymers,[2] charge-transfer complexes,[3] chalcogenide glasses,[4,5] amorphous silicon,[6] and substitutionally disordered molecular crystals.[7]

The theoretical work has been characterized by increasingly sophisticated approaches to deal with the simultaneous presence of spatial, temporal, and energetic disorder. These approaches include continuous-time random walk models (CTRW),[8] effective-medium theories,[9] Monte Carlo simulations,[10] and models of diffusion in restricted and fractal geometries.[11] Despite the wealth of experimental and theoretical work in this field, many fundamental questions remain unanswered. For example, is the disorder in these different types of amorphous systems in some sense equivalent, or are there distinguishable classes of disorder just as there are distinguishable classes of crystalline order? For each of the systems described above, what is the best macroscopic theoretical description? It has been claimed[12] that the effective-medium approach should be best at describing transport dominated by the hopping process, whereas the CTRW approach should be best for systems dominated by the trapping step. On the other hand, it has been stated elsewhere that multiple-scattering theories, such as the effective-medium approximation, can never be completely effective at dealing with disorder since theories of this type attempt to model a disordered system by approximating it with a homogeneous system.[13]

One would also like to understand the specific relationship between the macroscopic theoretical approaches mentioned above and the microscopic details of the charge-transport process. These microscopic details might include the fractal (or nonfractal) nature of the disorder and the relative importance of the hopping, trapping, and detrapping steps.

In the work described here, we chose to use the polyvinylcarbazole (PVK) system as an experimental vehicle for studying the questions posed above. We have also chosen to compare the experimental results that we have obtained with the predictions of the CTRW model. The PVK system was chosen in part because previous experimental results seemed to suggest that the CTRW theory needed to be modified in several ways to account for charge transport in PVK.[14] Contrary to these earlier results, we show here that hole transport in PVK, under carefully defined and controlled experimental conditions, is a very good example of a dispersive transport system within the CTRW theoretical context and within the time scale of our experiments. Also we emphasize the extreme sensitivity of the experimental results to sample preparation and later handling. A preliminary discussion of some of these results has been given elsewhere.[15]

II. THE CONTINUOUS-TIME RANDOM WALK MODEL

For charge-carrier transport in amorphous photoconductors, the most frequently used theoretical approach is the CTRW model of Scher and Montroll.[16] This model assumes that the transport of charge through the amorphous material is governed by a hopping rate W with a functional form similar to

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

where r is the distance between hopping sites, r_0 characterizes the range of the interaction responsible for hopping, and ΔE is the activation energy for hopping. k and T are Boltzmann's constant and the temperature, respectively. In an ordered crystal, W is a constant for carrier motion along a particular direction since r_0 and ΔE are constants from site to site. The hopping time distribution is thus exponential:

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

Ordered systems are said to exhibit *Gaussian transport* because of the Gaussian nature of the charge-carrier wave packet moving through the material. Charge trans-

©1989 The American Physical Society

port in an anthracene crystal has been shown to be an excellent example of this type of transport.[17]

In a disordered system both r_0 and ΔE can vary in a statistical fashion. This variation leads to a wide distribution of W's resulting in a continuous range of hopping times whose variation can extend well into the experimental time scale. In this case, Scher and Montroll have postulated that the hopping time distribution can be asymptotically expressed in an algebraic form:

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

In this expression α quantitatively describes the extent of the disorder; the smaller α (between 0 and 1), the greater the disorder. This type of transport has been called *dispersive transport.*

Experimentally, charge-carrier transport in photoconducting systems is most conveniently investigated using the time-of-flight (TOF) technique.[18] In a typical TOF experiment a sheet of charge is created at one face of the sample by a strongly absorbed pulse of radiation. Under the influence of an applied external electric field, the sheet of charge is swept through the sample finally leaving the system at the opposite electrode. One measures the current so produced as a function of time and attempts to relate the observed pulse shape to theoretical predictions.

For TOF experiments, the CTRW theory makes several clear predictions.

(a) The current transients can be described by two distinct algebraic time dependences. 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 at a time t_{tr}, defined as the carrier transit time, the functional form changes and becomes

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

(b) A universal master plot can be created if both the current and the time are normalized with respect to t_{tr}. The universal plot should be obtained regardless of the magnitude of the externally applied voltage.

(c) The transit time has the following functional form:

$$t_{\text{tr}} \propto \left[\frac{L}{l(E)}\right]^{1/\alpha} \exp\left[\frac{\Delta_0}{kT}\right] , \tag{6}$$

where L is the sample thickness, Δ_0 a hopping activation energy, and $l(E)$ an electric-field (E) dependent average hopping distance. Of particular importance in this expression is the explicit dependence of the transit time on thickness.

Measurements of the shape of the TOF curve, its universality, and the thickness dependence of the transit time should thus be able to distinguish Gaussian transport from dispersive transport in the CTRW scheme. Experiments to investigate this issue have been made on a wide variety of amorphous systems.[2,4] As_2Se_3 seems to be a nearly ideal example of an amorphous system exhibiting dispersive transport.[5] On the other hand, experimental results seemed to show that PVK was not a good example of dispersive transport in the Scher-Montroll sense, even though it could be shown that the carrier transport (by holes in this system) was clearly not Gaussian.[14] In PVK it was found necessary to use a different value of α depending on whether one was describing the initial part of the current transient [Eq. (4)] or the final part [Eq. (5)]. Scher and Montroll predict that a single value should suffice. Also, no thickness dependence was observed.[19]

III. EXPERIMENTAL

A. Sample preparation and experimental apparatus

Figure 1 shows the particular experimental embodiment of the TOF technique that we used. The strongly absorbed light pulse was provided at 337 nm by a 10-ns, 9-mJ Molectron UV-24 N_2 laser. This wavelength is substantially absorbed and the holes created within 0.1 μm of the irradiated PVK surface. Our sample configuration consists of an aluminized Mylar® sheet through which the sample is irradiated, an approximately 10-μm layer of PVK, and a rear electrode formed using Ag epoxy. Evaporated Ag was also tried as a rear electrode material with no discernible effect on the experimental observations. The optical density of the Mylar® plus aluminum layer is 1.33 at 337 nm. The laser light was focused down to a 0.4-cm^2 spot. This provided, at full intensity, an illumination on the PVK of 0.12 MW/cm^2. Experiments were actually performed with light attenuated by neutral-density filters to a power density of about 0.1 W/cm^2. Quantum yields for charge generation varied with temperature and with the applied electric field but were generally in the 10^{-3}–10^{-4} range. The holes may

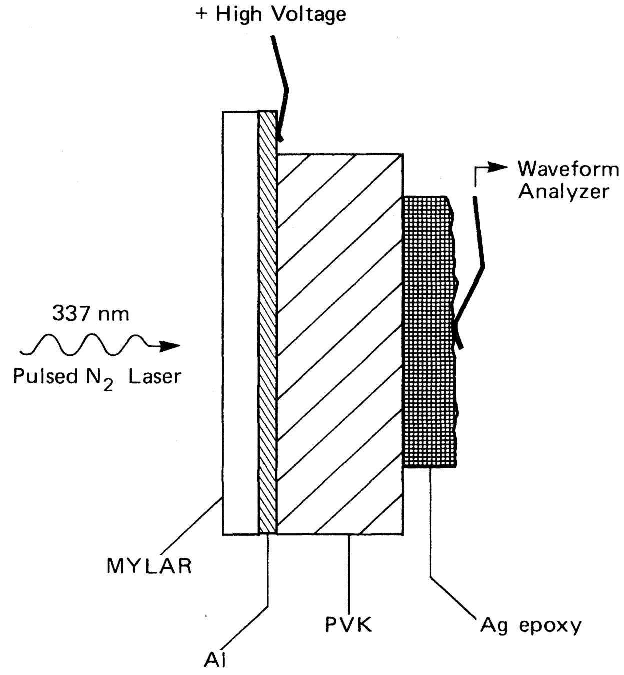

FIG. 1. Sample configuration used for the TOF experiment.

be created by photogeneration in the PVK, by photoinjection from the oxidized Al, or by a combination of both processes. For our present purposes the details of the charge generation step are not important. Typically dark current values of less than 0.02 nA were measured for the experiments done at 20 °C.

The PVK (Luvican® from BASF) was extensively purified by dissolving it in chloroform and precipitating by dropwise addition into boiling methanol. The precipitation process was carried out at least five times. PVK samples purified in this way exhibited no traces of anthracene impurity when analyzed by absorption and by high-performance liquid chromotography (HPLC). The importance of polymer purity in systems such as these has recently been emphasized by Yuh and co-workers.[20] In a different polymer system, they have shown that the transport can go from dispersive to Gaussian as the polymer is made "purer" by the removal of intentionally incorporated shallow traps.

The sandwich sample structure was prepared by the doctor blade technique from a chloroform solution. Typical thicknesses of samples prepared in this way were 10–15 μm. The samples were dried in a vacuum oven at 350 K for at least 12 h. Care was taken not to expose the PVK solutions to light from the time they were initially prepared by precipitation until they were taken from the vacuum oven. The PVK films were prepared, dried, and stored in the dark to avoid photo-oxidation.[21] The method of preparing the PVK samples is important and there is some evidence that the experimentally observed hole transient shapes can vary significantly depending on the details of the preparation method.[22]

Figure 2 shows the data collection setup that was used to obtain the results reported here. This experimental arrangement was particularly useful at the low light (and thus signal) levels that we found necessary to achieve reliable experimental results. Data were recorded using a digital waveform analyzer (Data Precision 6000) and fed directly to a computer (IBM PC/AT) for storage, analysis, and display. This arrangement gave us a horizontal and vertical dynamic range of over 4 orders of magnitude. We could thus record data with single-shot sensitivity of less than 1 μV. In addition by using the pretriggering capabilities of the waveform analyzer we could obtain an accurate baseline. This is extremely important since the data must be displayed on a log-log plot for analysis. Any small baseline inaccuracy will distort the observed current transient curves. Considerable uncertainty could be introduced in the results, particularly in the determination of α from the slope of the final portion of the transient, by a small nonzero background. The sample was held at constant temperature of ±1 °C inside a controlled temperature chamber.

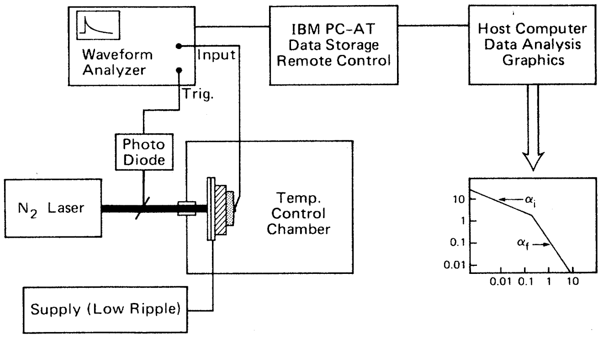

FIG. 2. Block diagram of detection equipment used in our TOF experimental setup.

Most previous workers have attempted to clear the sample of accumulated trapped charge from flash to flash by removing or reversing the voltage and flashing the sample. We have found that this is totally inadequate and results in a measurable slowly decaying dark current which when superimposed on top of the transient distorts the experimental results. The best way to minimize the effect of this dark current is to wait between flashes until the current has decayed to a negligible value with the original voltage still across the sample. Typically this requires a waiting period of at least 45 min. All of our results were determined after waiting at least this length of time between laser shots.

B. Sensitivity to exciting light intensity

An unusual and yet unexplained feature of hole TOF transients in PVK is their extreme sensitivity to light intensity. We have found it necessary to work with light levels more than ten times weaker than those that one would choose to work with from considerations of space-charge effects alone.[23(a)] The sample configuration shown in Fig. 1 has an effective capacitance of about 500 pF. For a typical applied external voltage of 200 V, this implies a charge stored across the capacitor created by the sample cell of about 10^{-7} C. Conventional space-charge effects should be negligible in these TOF experiments for hole concentrations ten times or more below this stored charge level. In fact, we find that one must go at least 1 additional order of magnitude in carrier concentration below that before obtaining reliable experimental information.[15] Typical hole concentrations produced during one of the experiments discussed below were in the 10^{-9}–10^{-10}-C range. Similar light intensity effects have been observed in As_2Se_3 by Gibson and Kastner.[23(b)]

Figure 3 shows a typical hole transient in PVK taken at low light intensity. The algebraic dependence of initial and final slopes is shown. Clearly, within experimental uncertainty, only a single value of α is found necessary to describe this transient. The experimental meaning of the transit time t_{tr} is also made clear in the figure.

Table I describes a set of experiments designed to show what can occur when one uses too much light. First a reference transient at low light intensity was recorded. In this case the initial value α_i and the final value α_f were equal within the experimental uncertainties. The transit time t_{tr} was found to be 50 ms. Next a laser pulse roughly 100 times more intense than the initial pulse was used to produce a transient. After this intense blast, another transient was recorded at low light intensity. The results of this experiment are listed as the 0 time values in Table I. Clearly $\alpha_i \neq \alpha_f$ now and t_{tr} has also increased consid-

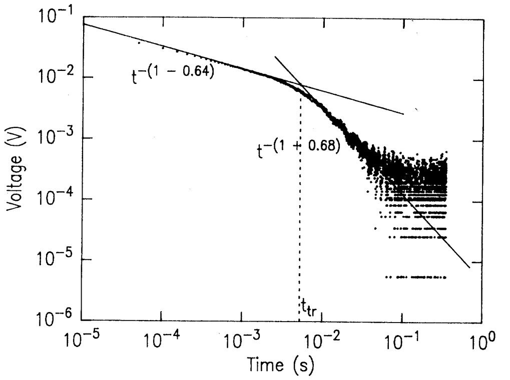

FIG. 3. Typical TOF transient plotted on a log-log scale. The curve is the average of four experimental measurements made with a 45-min relaxation time in between the 1-μJ, 10-ns laser shots. The algebraic time dependences as derived from a least-squares fitting routine are also shown. The dashed line indicates the transit time. The measurement was made with 300 V applied across the 550-pF, 10-μm-thick sample at $+10\,^{\circ}$C. The sampling period of the DP 6000 was 50 μs. To derive the actual voltages, the readings along the ordinate should be divided by 20 to compensate for the preamp amplification.

erably. (It is important to emphasize at this point that by using the terms α and t_{tr}, we do not mean to imply that the transients observed after intense illumination necessarily obey the CTRW model. These parameters, in this context, are merely a simple means to keep track of changes in the transient shape.) Even after 25 h, the transient has not completely returned to its original shape.

Figure 4 illustrates the recovery of the transit time after intense pulsed irradiation. The dotted line in the figure is a fit of the experimental data to a stretched exponential of the form

$$t_{tr}=C\exp\left[-\left[\frac{t}{\tau}\right]^{\gamma}\right]+55\ \text{ms}, \tag{7}$$

where all three adjustable parameters are allowed to vary independently. This form is typical of ones that characterize relaxation processes in amorphous systems.[24] It is interesting to note that the value of γ obtained from the fit is equal to the value of α obtained from the transients although the fit, particularly at longer times, is not good. If the relaxation process responsible for the recovery of the transit time has an event time distribution of the form of Eq. (3), it can be shown that α and γ may indeed be identical[25] and relate to the underlying state of disorder in the system.

TABLE I. Effect of high pulsed-light intensity on transient shape.

Time	α_i	α_f	t_{tr} (ms)
Ref.	0.64	0.69	50
0	0.62	0.48	100
5	0.54	0.55	75

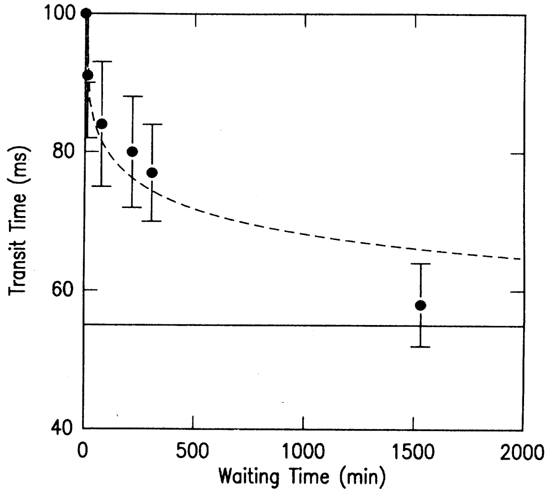

FIG. 4. Plot of the effect of excitation by high light intensity on the measured transit time. The solid horizontal line at 55 ms is the value of t_{tr} found before intense illumination. The dashed line is a fit of Eq. (7) to the experimental data. Fitting parameters were $C=48.2$ ms, $\tau=408$ min, and $\gamma=0.6$.

These results clearly demonstrate the necessity of keeping the charge-generating light pulse as low as possible. It is clear that, depending on the amount of light used to make the experimental measurements, an apparent dependence of the quantities α and t_{tr} on the history of illumination can be obtained. We have previously shown[15] how the light intensity can affect the measured value of t_{tr}.

C. Error handling and analysis of the data

Because of the extreme sensitivity of the experimental results to sample handling conditions, the sensitivity to light intensity described above, and the consequent need to work at as low a light intensity as possible, the manner of analyzing the data is of critical importance. In this section, the approach that we have used to analyze the transients is described.

Referring to Fig. 3, one can easily see that there is a considerable amount of noise associated with the final portion of the transient. Some of the voltage values are actually negative. To handle these negative values in a consistent way, the following approach was used.

(a) The data were looked at in a log-log plot and two time ranges were chosen for the evaluation of α_i and α_f.

(b) A fit to the algebraic form of Eqs. (4) and (5) was made over the chosen time regions. The fit was done on the raw data, not on a log-log version of the data. This avoided problems with negative voltage values.

(c) The transit time was determined from the intersection of the two lines generated from the fit, as shown in Fig. 3.

Small variations (less than 10%) in the values of α and t_{tr}

could be obtained depending on the precise ranges chosen for the fitting. These errors were much less than variations from experiment to experiment and were considered acceptable.

As mentioned above, there is considerable shot-to-shot variation in the value of α_f. In a series of 78 measurements on a single sample at room temperature (23 °C) over a period of several days, the value of α_i was found to be 0.61 with a standard deviation of 0.08. For the same set of experiments, α_f was found to be 0.56 with a standard deviation of 0.19. These errors are considered upper limits. Experiments conducted on a single sample over a few hours showed considerably smaller standard deviations. There was a correlation between values of α_i which were outside the standard deviation range and values of α_f which were similarly off. In the results reported here, we have discarded all experiments which resulted in α_i values that were outside the standard deviation range mentioned above. The curves that were analyzed were obtained by averaging together results from at least three consecutive shots.

IV. RESULTS

A. Dispersive nature of the transport

In Sec. II three experimental tests for dispersive transport were listed; algebraic transient decay with a single value of α, universality, and an α-dependent sample-thickness dependence. In this section, we will show that hole transport in PVK exhibits all three of these characteristics.

Figure 3 shows that the transient values obtained from the initial and final portions of the curve are, within experimental error, equal. Figure 5 compares the temperature dependence that we have observed for α_i and α_f with values obtained by Pfister and Griffiths.[14] Our results show that $\alpha_i = \alpha_f$ and that α is, within experimental error, temperature independent. The error limits shown in Fig. 5 are for experiments on a single sample in which $\alpha_i \approx \alpha_f$. As described in Sec. III C, if samples in which $\alpha_i \neq \alpha_f$ are included, the limits of experimental error increase. This larger error is indicated for the point at +20 °C in Fig. 5.

There are several possible reasons for the discrepancies between the results reported here and those obtained by Pfister and Griffiths. One obvious possibility is that the earlier work was done with too much exciting light intensity. This would distort the values of α obtained as we have previously described and could also result in a temperature dependence. If the exciting light intensity dependence is due to the number of carriers produced, the carrier concentration can also be increased, keeping the light intensity constant, by increasing the temperature. It is well known that the number of free carriers generated is a function of temperature.[26] It is also possible, of course, that differences in the physical nature of the PVK samples themselves could result in the observed differences in the transient shapes.

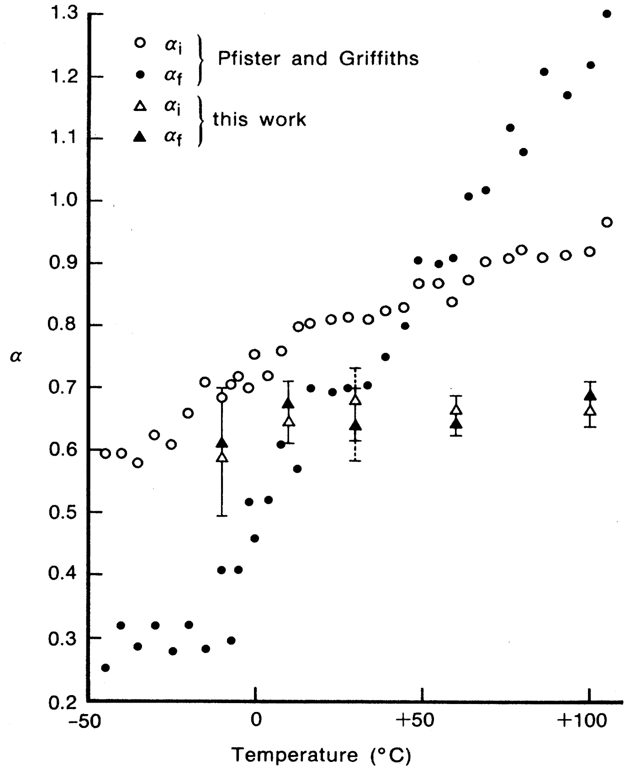

FIG. 5. Comparison of the α's taken from Ref. 14 with the α's obtained in this study. The solid error bars represent deviations for four runs with a single sample over a short period of time. The larger dotted error limits refer to the measurements over several days described in Sec. III C.

Universality, as predicted by the CTRW model, is demonstrated in Fig. 6. Because of the temperature independence of α, we observe universality not only for several different voltages, but also at different temperatures as well.

In Fig. 7 the thickness dependence of the transit time is shown. The solid line is a curve of slope $1/\alpha$ where α was fixed at the value of 0.6 found from the shape of the

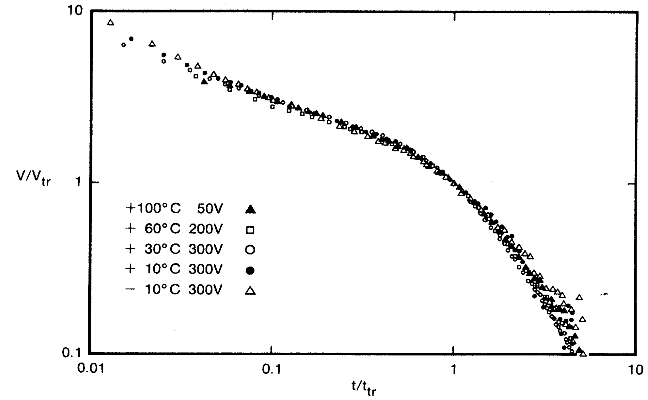

FIG. 6. Universal master plot of transients obtained at several temperatures as well as voltages. The mobilities μ given in the figure are derived from $\mu = L^2/Vt_{tr}$. The sample thickness $L = 10$ μm; V is the applied voltage and t_{tr} is the transit time defined in Fig. 3.

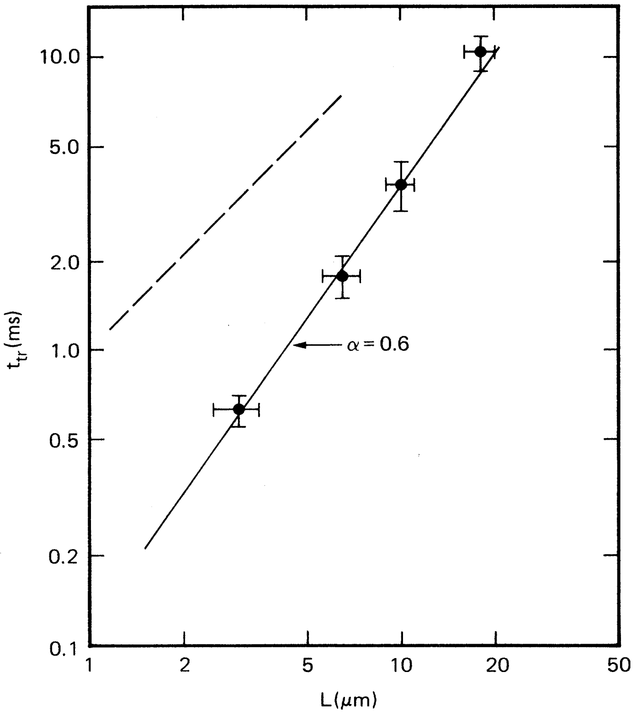

FIG. 7. The sample-thickness dependence of the transit time. The solid line is drawn with slope $1/\alpha$, where α has the value of 0.6 determined from the transient shapes. The dashed line has a slope of 1. This is the slope value expected for nondispersive transport.

transient. The data are well described by the thickness dependence of Eq. (6). Also shown in the figure is a line with slope 1.0. This is the thickness dependence that one would expect if PVK exhibited nondispersive transport, i.e., a thickness-independent mobility.

The results presented in this section clearly indicate that hole transport in PVK is dispersive and obeys all of the predictions of the CTRW theory. This conclusion is in contradiction with earlier work that suggested that in some important respects PVK deviated from the CTRW predictions.[14]

B. Electric field dependence of the transit time

The electric-field and temperature dependence of the transit time or mobility has been used by many workers in the past to gain some insight into the microscopic nature of the charge-transport process in amorphous systems. Here the mobility is defined in the conventional way as

$$\mu=\frac{L}{Et_{\mathrm{tr}}} . \tag{8}$$

The current theoretical situation has been summarized recently by Stolka *et al.*[27] Schein and co-workers[28] have shown that in some molecularly doped polymer systems, charge transport does not seem to agree with any of the accepted theoretical models. In this section, we compare measurements of the electric field dependence of the transit time in PVK with several of these models. We have been unable to obtain reliable experimental data over a wide enough temperature range to be able to compare the experimental temperature dependence with theoretical expectations.

TABLE II. Electric field dependence of transit time.

Theoretical model	Electric field dependence	Ref.
Poole-Frenkel	$\frac{1}{E}\exp(-\beta_{\mathrm{PF}}E^{1/2})$	29
Multipole	$\frac{1}{E}\exp(-\beta_{Mn}E^{n/n+1})$	
Statistical hopping	$\exp(-\beta_{\mathrm{SH}}E)$	30
Kinetic	$\sinh(\beta_K E)^{-1/\alpha}$	31

Table II lists the functional dependence of the transit time on the electric field predicted by several of the models. The Poole-Frenkel model considers the electric field dependence as being due to escape from a Coulomb well.[29] This approach can be easily extended to include escape from a multipolar well as indicated in the table. In the table, $n=2$ refers to a dipole potential, for example. Bässler and co-workers[30] have developed a model based on their experience with Monte Carlo simulations of statistical hopping transport within a Gaussian density of energy levels. They obtain an exponential dependence of the transit time on the electric field and support their theoretical predictions with comparison to experimental results on several polymeric systems. The final functional form for the electric field dependence is due to Pfister.[31] Following earlier work by Bagley,[32] Pfister began with Eq. (6) and tried to deduce the electric field dependence by examining the $l(E)$ factor. The approach is conceptually very straightforward. The electric field dependence arises from the asymmetry in the energy barrier that the particle must overcome in hopping with or against the external electric field.

Figure 8 shows the mobility as a function of the root of the electric field as might be expected from the Poole-Frenkel model. This model makes a very clear prediction

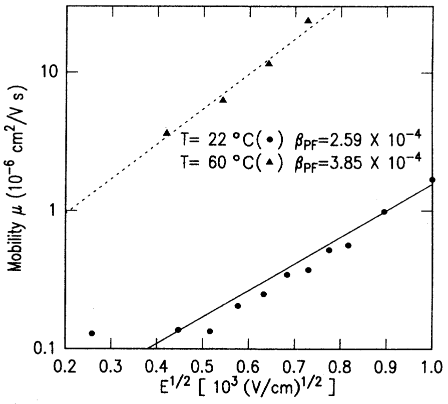

FIG. 8. Fit of the electric field dependence of the mobility to the functional form expected in the Poole-Frenkel model (see Table II).

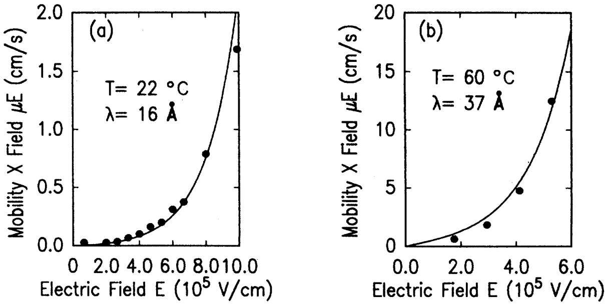

FIG. 9. Fit of the electric field dependence of the mobility to the functional form expected from the kinetic model (see Table II) at two temperatures (a) 22 °C and (b) 60 °C. The value of the average hopping distance λ is also shown in the figure.

of the value of β_{PF} to be expected:

$$\beta_{PF}=\left[\frac{e^3}{\pi K\epsilon_0}\right]^{1/2}, \tag{9}$$

where K is the dielectric constant, e is the electron charge, and ϵ_0 is the permittivity of free space. For a dielectric constant of 3.0, the expected value is $\beta_{PF}=4.4\times10^{-4}$ eV/(V/cm)$^{1/2}$. As can be seen from the figure, our value is close to that expected and in very good agreement with the value of 2.4×10^{-4} recently obtained by Muller-Horsche *et al.*[33]

Figure 9 is a comparison of our experimental results with the predictions of the kinetic model defined in Table II. The value of α was fixed at 0.6 for these fits. The kinetic model relates the value of the coefficient β_K to the average hopping distance λ:

$$\beta_K=\frac{e\lambda_0}{2kT}\ . \tag{10}$$

The values of λ_0 obtained at the two temperatures and indicated in the figure are plausible, and the hopping distance increases with temperature as might be expected. For comparison, Pfister found values of 40–50 Å for As_2Se_3.[31]

The data can be fit to the multipolar and statistical hopping functions as well. Within the temperature regime that we investigated, the functional forms in Table II are not distinguishable. To distinguish among these theories, measurements at lower electric fields need to be made. Unfortunately this is just the experimental regime in which the signal becomes weak and the results become unreliable.

V. DISCUSSION

The extreme sensitivity of the hole transients in PVK to the amount of light absorbed or equivalently to the number of charges created remains a puzzle. We have considered and rejected several possible explanations. Clearly the effect is not a space-charge effect in the conventional sense, since the distortion of the transient shape is observed with carrier concentrations well below the values where one needs to be concerned about this phenomenon. It cannot be due to dynamic electrical polarization effects caused by the passage of the charge carrier sheets through the sample. It can be shown that the polarizations behind and ahead of the sheet of charge exactly cancel each other, leading to no net effect.

We have earlier proposed that the distortion of the transient shape might be due to Coulomb spreading of the charge-carrier packet created by light absorption.[15] While simulations have shown that in principle this effect might distort the pulse shape, it is not clear whether the distortion would yield the shapes actually observed.[34] It is also difficult to imagine how this explanation could explain the very slow recovery of the system after intense illumination indicated in Fig. 4.

Another possibility is the delayed release of surface charge.[5] If the surface charge concentration were intensity dependent one might expect to see an intensity-dependent transient shape. Although all of the experiments reported here were done with an oxidized Al electrode, we have also done experiments with a chromium irradiated electrode and observed very similar light intensity effects. This does not eliminate the possibility that surface charge effects might be occurring. It merely indicates that the nature of the illuminated electrode does not appear to be a critical factor.

Charge-induced local structural changes or photoinduced or charge-induced chemical reactions[21] might also explain the results. In particular, the long recovery time of an irradiated sample might be due to relaxation back to the original structure or reversing of a chemical reaction.

Another interesting feature of the results presented here is the apparent temperature independence of the parameter α. Multiple trapping models indicate that α should depend linearly on temperature.[4] Our data are not inconsistent with a slight temperature dependence of this form. The value of α is ultimately determined by an ensemble of transition rates each having the functional form of Eq. (1). A truly temperature-independent α implies that the Boltzmann factor in this equation is unimportant over the ensemble. If this is the case, then the carrier hopping dynamics are determined only by the spatial term in Eq. (1). In other words, charge-carrier transport in PVK is determined primarily by geometry. Blumen *et al.*[35] have given an analysis of the geometric effects of carrier hopping in a disordered system. They have tried to divide the effects of the geometric disorder into two parts: temporal and spatial. The temporal disorder is characterized by a parameter χ describing the hopping time fluctuations due to the disorder. Since χ is related to Eq. (1), one might expect it to be temperature dependent. The spatial disorder is described by a parameter β that depends only on the geometry of the lattice, and as long as the underlying geometry does not change, β should be temperature independent.

Blumen *et al.* have shown that the parameter α can be written

$$\alpha(T)=\chi(T)\beta\ , \tag{11}$$

where β is related to the fractal nature of the disordered system. For a normal Euclidean lattice χ and α are iden-

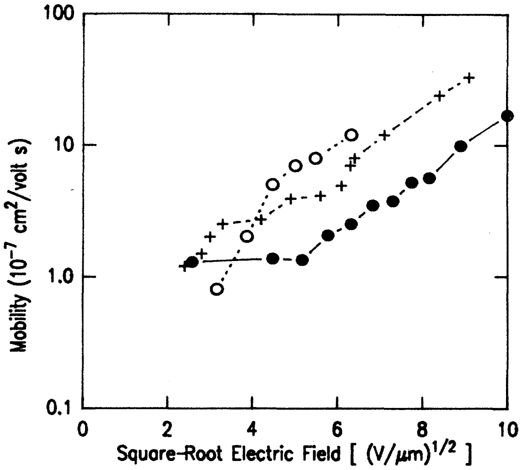

FIG. 10. Comparison of electric-field-dependent mobility measurements for PVK by different research groups: ●, this work; ○, Ref. 33; +, Ref. 36.

tical. It is not clear in practice that one can make such a clean separation between spatial and temporal manifestations of disorder. The point in the present context is that there is a strictly geometric and temperature-independent component of α consistent with our experimental observations.

Finally, a few words are in order concerning the difficulty of determining the exact functional form for the electric field dependence of the transit time. Figure 10 shows mobility versus electric field measurements for PVK made by three different experimental groups.[33,36] The first thing to note is that at higher electric fields the slopes of the lines are more or less equal. This means that, when one tries to determine values of β for any of the models summarized in Table II, one will obtain more or less equal values for each of the three sets of experimental data. The results only began to deviate from each other at low electric fields. Unfortunately this is just the region where a distinction between the functional forms of Table I can be made. Another disturbing thing about the results is their disagreement as to the absolute value of the mobility at any single electric field value. This disagreement may have several origins. It may be due to the extreme sensitivity of the samples to experimental handling and exposure to light, as discussed above, or it may be related to differences in the microscopic structure of the PVK itself. There is some evidence for this latter explanation in the work of Haarer and co-workers.[22] They find quite different transient shapes for PVK depending on the method of sample preparation.

VI. CONCLUSIONS

In this paper we have shown that PVK is an excellent example of a system that obeys the CTRW model of charge-carrier transport. The value of the parameter α that expresses the degree of disorder is found to be temperature independent within the error limits of our experiment over the range -10 to $+100\,^{\circ}$C. This implies that hole transport in PVK is determined primarily by the geometry of the polymer system.

The electric field dependence of the transit time has been measured and compared with theoretical predictions. The results seem to agree well with several of the theoretical models. In particular, both Poole-Frenkel and kinetic models yield experimental fitting parameter values that are physically reasonable. To distinguish among the various models listed in Table II, one needs to obtain data in the experimentally difficult low-electric-field regime.

Finally, we emphasize, as we have done previously,[15] the extreme sensitivity of these transient shapes on illumination intensity. One must work with exciting light intensities more than an order of magnitude lower than expected from consideration of space-charge effects.

ACKNOWLEDGMENTS

The careful sample preparation work of James Miller is gratefully acknowledged. We have benefitted from technical discussion with J. Campbell Scott.

---

[*] Present address: Philips Research Laboratory, P.O. Box 8000, NL-5600 JA Eindhoven, The Netherlands.

[1] H. Bässler, Phys. Status Solidi B **107**, 9 (1981); H. F. Kauffmann, W.-D. Weixelbaumer, J. Buerbaumer, A-M. Schmoltner, and O. F. Olaj, Macromol. **18**, 104 (1985); G. Peter, H. Bässler, W. Schrof, and H. Port, Chem. Phys. **94**, 445 (1985).

[2] J. Mort and G. Pfister, in *Electronic Properties of Polymers,* edited by J. Mort and G. Pfister (Wiley, New York, 1982), p. 215; J. Mort and G. Pfister, Polym.-Plast. Technol. Eng. **12**, 89 (1979).

[3] W. D. Gill, J. Appl. Phys. **43**, 5033 (1972).

[4] G. Pfister, Phys. Rev. Lett. **36**, 271 (1976); G. Pfister and H. Scher, Adv. Phys. **27**, 747 (1978).

[5] G. Pfister and H. Scher, Phys. Rev. B **15**, 2062 (1977); M. Abkowitz and H. Scher, Philos. Mag. **35**, 1585 (1977).

[6] W. E. Spear and P. G. LeComber, Philos. Mag. B **52**, 247 (1985).

[7] P. N. Prasad, J. R. Morgan, and M. A. El-Sayed, J. Phys. Chem. **85**, 3939 (1981); J. R. Morgan and M. A. El-Sayed, *ibid.* **87**, 2178 (1983).

[8] E. W. Montroll and B. J. West, in *Fluctuation Phenomena,* edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1979).

[9] M. Lax and T. Odagaki, in *Macroscopic Properties of Disordered Media,* edited by R. Burridge, S. Childress, and G. Papanicolaou (Springer, Berlin, 1982), Vol. 154, p. 148; M. Grünewald, B. Pohlmann, B. Movaghar, and D. Würtz, Phi-

los. Mag. B **49**, 341 (1984); P. R. Parson and R. Kopelman, J. Chem. Phys. **82**, 3692 (1985).

[10]M. Silver, K. S. Dy, and I. L. Huang, Phys. Rev. Lett. **37**, 1360 (1976); J. M. Marshal, Philos. Mag. B **36**, 959 (1977); **38**, 335 (1978); B. Ries and H. Bässler, Phys. Rev. B **35**, 2295 (1987); B. Ries, H. Bässler, M. Grünewald, and B. Movaghar, *ibid*. **37**, 5508 (1988).

[11]R. Rammal and G. Toulouse, J. Phys. (Paris) Lett. **44**, L-13 (1983); A. Blumen, J. Klafter, and G. Zumofen, J. Chem. Phys. **84**, 1397 (1986).

[12]G. A. Niklasson, J. Appl. Phys. **62**, R1 (1987).

[13]A. Blumen, J. Klafter, and G. Zumofen, *Optical Spectroscopy of Glasses* (Reidel, Dordrecht, 1986), p. 199.

[14]G. Pfister and C. H. Griffiths, Phys. Rev. Lett. **40**, 659 (1978).

[15]F. C. Bos and D. M. Burland, Phys. Rev. Lett. **58**, 152 (1987); D. M. Burland and F. C. Bos, *Physics of Amorphous Semiconductor Devices* [Proc. SPIE **763**, 95 (1987)].

[16]H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).

[17]N. Karl, E. Schmid, and M. Seeger, Z. Naturforsch. **25A**, 382 (1970).

[18]W. E. Spear, Proc. Phys. Soc. London, Sect. B **70**, 669 (1957); **76**, 826 (1960); R. G. Kepler, Phys. Rev. **119**, 1226 (1960); O. H. LeBlanc, J. Chem. Phys. **33**, 626 (1960).

[19]A. R. Tahmasbi and J. Hirsch, Solid State Commun. **34**, 75 (1980).

[20]H. J. Yuh, D. Abramsohn, and M. Stolka, Philos. Mag. Lett. **55**, 277 (1987).

[21]A. Itaya, K. Okamoto, and S. Kusabayashi, Bull. Chem. Soc. Jpn. **52**, 2218 (1979).

[22]D. Haarer (private communication).

[23](a) A. C. Papadakis, J. Phys. Chem. Solids **28**, 641 (1967); D. J. Gibbons and A. C. Papadakis, *ibid*. **29**, 115 (1968); (b) D. D. Gibson and M. A. Kastner, in *Disordered Semiconductors*, edited by M. A. Kastner, G. A. Thomas, and S. R. Ovshinsky (Plenum, New York, 1987), p. 237.

[24]J. Friedrich and A. Blumen, Phys. Rev. B **32**, 1434 (1985).

[25]W. H. Hamill and K. Funabashi, Phys. Rev. B **16**, 5523 (1977); A. Plonka, J. Kroh, W. Lefik, and W. Bogus, J. Phys. Chem. **83**, 1807 (1979).

[26]R. H. Batt, C. L. Braun, and J. F. Hornig, J. Chem. Phys. **49**, 1967 (1968).

[27]M. Stolka, J. F. Yanus, and D. M. Pai, J. Phys. Chem. **88**, 4707 (1984).

[28]L. B. Schein, A. Rosenberg, and S. L. Rice, J. Appl. Phys. **60**, 4287 (1986).

[29]J. Frenkel, Phys. Rev. **54**, 647 (1938).

[30]H. Bässler, G. Schrönherr, M. Abkowitz, and D. M. Pai, Phys. Rev. B **26**, 3105 (1982).

[31]G. Pfister, Philos. Mag. **36**, 1147 (1977).

[32]B. F. Bagley, Solid State Commun. **8**, 345 (1970).

[33]E. Muller-Horsche, D. Haarer, and H. Scher, Phys. Rev. B **35**, 1273 (1987).

[34]F. C. Bos (unpublished).

[35]A. Blumen, J. Klafter, B. S. White, and G. Zumofen, Phys. Rev. Lett. **53**, 1301 (1984).

[36]M. D. Tabak, D. M. Pai, and M. E. Scharfe, J. Non-Cryst. Solids **6**, 357 (1971).