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Temperature Dependence of Transient Hole Hopping Transport in Disordered Organic Solids: Carbazole Polymers

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Nondispersive hopping transport has been observed in disordered poly(N-vinylcarbazole) (PVK) but not in the related polymer 3Br-PVK. The results demonstrate that a hopping-time distribution $\psi(t) \sim t^{-(1+\alpha)}$ can account for the transit-time dispersion in a limited temperature range but that more complicated $\psi(t)$'s are necessary to model the results in a broader temperature range. The subtle relation between sample morphology and transient dispersion is demonstrated.

The Scher-Montroll formalism[1] of continuous-time random walk (CTRW) successfully accounts for many novel features of dispersive (non-Gaussian) transport which, in some temperature range, is observed in time-of-flight experiments in most disordered solids.[2-7] For a-As_2Se_3 transient hole transport remains dispersive over the entire experimental temperature range 230–380 K and its features can be explained with a CTRW based upon an event time distribution function $\psi(t) \propto t^{-(1+\alpha)}$ where the disorder parameter α assumes a value between zero and unity.[1,2] The temperature insensitivity of the hole transit-time dispersion in a-As_2Se_3 requires $\alpha \sim$ const.[2] It has been argued that a temperature-independent α indicates hopping rather than multiple-trapping transport and that the dominant source for the transit-time dispersion is associated with fluctuating hopping-site distances rather than a distribution of activation energies.[1,2] In fact, a consistent numerical description of the transport data is obtained for trap-modulated hopping transport[2] (trap-controlled hopping[5]).

Different temperature behavior is observed for transient hole transport in a-Se.[3] The hole transients, which at room temperature are Gaussian, become progressively more dispersive as the temperature is lowered and below ~ 180 K approach the non-Gaussian features typical of a-As_2Se_3. Obviously a $\psi(t)$ more complicated than for a-As_2Se_3 is needed to account for these observations. That increase in complexity invariably leads to an increase of the number of adjustable parameters and, indeed, excellent agreement is obtained in terms of a generalized multiple-trapping formalism based on three traps (nine parameters).[8] The latter formalism is mathematically equivalent to the CTRW theory.[8,9] Interestingly the parameters derived from this model suggest a hopping process rather than transport in extended states.[8] However, as for a-As_2Se_3, the identification of the microscopic transport process remains somewhat ambiguous.

While the analysis of the hole transit-time data for a-Se and a-As_2Se_3 tends to indicate hopping transport, the issue has been raised recently as to whether hopping transport (at constant energy) *per se* can give rise to dispersive behavior as has originally been proposed by Scher and Montroll.[10,11] Specifically it is questioned whether fluctuating hopping-site distances alone can induce non-Gaussian transport behavior. However at the present time this issue has not been settled by a rigorous theoretical analysis although intuitively one expects that fluctuating distances contribute to the transit-time dispersion. Most of the criticisms have dealt with mean behavior and have not addressed the subleties associated with the few fluctuations from the mean that can cause non-Gaussian dispersion.[11] Given this scenario it appears highly desirable and timely experimentally to investigate dispersive transport in model systems where, *a priori*, the microscopic process is known to be hopping.

We have identified two closely related hopping systems, one of which exhibits temperature-dependent dispersive transport similar to a-Se while the other displays features comparable to a-As_2Se_3. The two systems, respectively, are the organic polymer poly(N-vinylcarbazole) (PVK), and bromine-substituted PVK with the bromine substitution on either the 3 or 6 position on the carbazole ring, 3Br-PVK. The reported time-of-flight studies clearly demonstrate that over a limited temperature range the Scher-Montroll CTRW based upon $\psi(t) \sim t^{-(1+\alpha)}$ can explain the transit-time data. However, to account for the data in the entire temperature range the $\psi(t)$ originally proposed for hopping transport is too limited. Furthermore we present the first evidence for nondispersive hopping transport in a disordered array of hopping sites and show that the observation of dispersive or nondispersive transport can depend on subtle differences in sample morphology.

The 10–15-μm-thick sample films were prepared by casting chloroform solutions of PVK and 3Br-PVK onto ball-grained Al plates. The films were dried in vacuum at 350 K for 24 h. The PVK was high-molecular-weight and relatively monodispersive material obtained by fractional precipitation from a solution of BASF Luvican M170 polymer.[12] 3Br-PVK was obtained by free radical polymerization of 3-bromo N-ethylcarbazole to obtain a high-molecular-weight polymer similar to PVK.[13] Transparent Al electrodes were vacuum deposited onto the films to provide the sandwich cells used in the time-of-flight experiments. Free holes were intrinsically photogenerated by a 4-nsec pulse of 3371-Å light derived from a N_2 laser.

Figure 1 shows an Arrhenius plot of the hole drift mobility in PVK and 3Br-PVK measured at 20 V/μm applied electric field as a function of temperature in the range 150–500 K. Also shown in Fig. 1 are representative hole-current traces $I(t)$ recorded at various temperatures. The two essential results to be noted from Fig. 1 are that (i) for both systems the activation energy remains well defined in the entire temperature range and (ii) for PVK the transient current indicates a transition from dispersive to nondispersive transport if the temperature is raised above ~420 K. In the same temperature range the dispersion of hole transport in 3Br-PVK decreases only little and clearly remains dispersive at the highest experimental temperature. The upper bound to the temperature range in these experiments is deter-

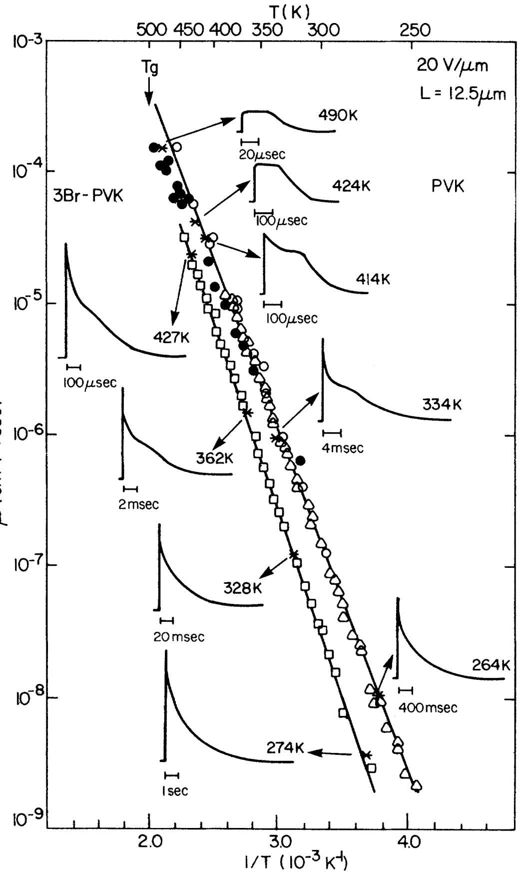

FIG. 1. Log μ vs $1/T$ for hole transport in PVK and 3Br-PVK current pulses for various temperatures are shown.

mined by the glass transition which occurs at ~ 500 K.

The results shown for PVK are similar to hole-transport data for a-Se[3] while those for 3Br-PVK resemble hole transport in a-As_2Se_3,[2] the main differences being the time frame of the transit times and, in the former case, the temperature of the transition from dispersive to nondispersive transport.

Dispersive transient currents $I(t)$ are commonly analyzed in plots of $\log I$ versus $\log t$.[2-4,7] For a CTRW based on $\psi(t) \propto t^{-(1+\alpha)}$, $I(t)$ exhibits the power dependences $t^{-(1-\alpha)}$ and $t^{-(1+\alpha)}$ for $t < t_T$ and $t > t_T$, respectively, where t_T is a measure of the transit time.[1] Hence, the value of the disorder parameter α can readily be determined from the $\log I$ versus $\log t$ plots. For the present analysis one conveniently defines α_i and α_f as the α values determined from the initial ($t < t_T$) and final ($t > t_T$) part of the hole transient. In terms of these parameters nondispersive transport can be characterized by $\alpha_i \cong 1$ and $\alpha_f \gg 1$ while for dispersive transport as described by Scher and Montroll $0 < \alpha_i (= \alpha_f) < 1$.

The inset of Fig. 2 shows current traces in logarithmic units of 355 K and 20 V/μm. The dashed lines indicate the power laws used to approximate the transient current in the time range typically extending from ~ $1/10\,t_T$ to ~ $10\,t_T$. In the main part of Fig. 2 the temperature dependence of the α values is plotted for PVK (lower part) and 3Br-PVK (upper part). The dominant observation to emphasize is that the Scher-Montroll result $\alpha_i = \alpha_f$ is indeed observed over some limited temperature range, viz. 315–335 K for PVK and 345–395 K for 3Br-PVK. Outside these temperature ranges $\alpha_i \neq \alpha_f$ where the two parameters have different temperature dependences. Hence, for both hopping systems a CTRW based upon an algebraic $\psi(t)$[1] is to limited to explain the transit-time dispersion even if α is allowed to be temperature dependent.[14]

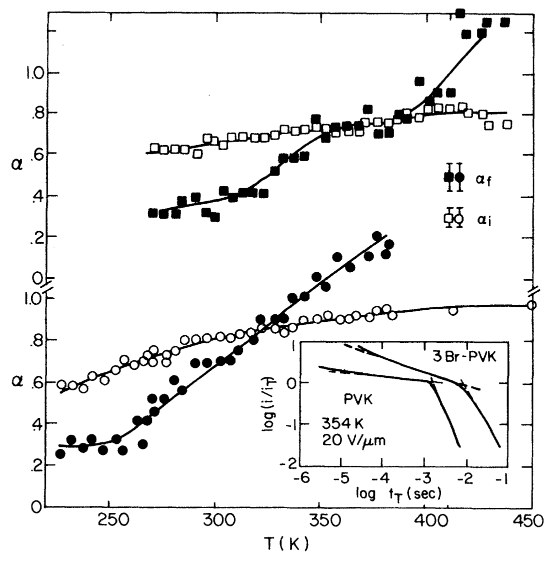

FIG. 2. $\alpha_i(T)$ and $\alpha_f(T)$ for PVK (lower part) and 3Br-PVK (upper part). The inset shows representative current traces in logarithmic units.

Comparing PVK with the brominated sample one notes that for 3Br-PVK α_i and α_f increase much more slowly with increasing temperature and that the final value of α_i is ~ 0.8 rather than 1.0 which characterizes nondispersive transport. The approach to nondispersive hole transport in PVK, indicated in Fig. 1, is clearly borne out by the α values shown in Fig. 2. This is the first incidence that nondispersive hopping transport has been reported for a disordered system. This could indeed indicate that, by itself, a fluctuation of hopping-site distances—as originally invoked to generate $\psi(t) \propto t^{-(1+\alpha)}$ and used to explain the transit-time data in a-As_2Se_3—is not sufficient to produce non-Gaussian transport. It should be emphasized, however, that only a suitable confluence of the system variables and the transit time will lead to non-Gaussian transport! It appears on the basis of Noolandi's[8] analysis of hole transport in a-Se, that a distribution of hopping distances *is* required—in addition to a distribution of hopping energies—in order to account for the entire temperature dependence of the transit-time dispersion in a-Se, in particular the transition from Gaussian to non-Gaussian transport.

A temperature-dependent dispersive can arise from fluctuating energy levels. In organic hopping systems where the localized sites are molecules (carbazole side groups in PVK) the transition matrix elements can exhibit a temperature dependence due to motional degrees of freedom of the constituent molecules or polarization shifts of molecular levels. Temperature-dependent overlap terms have indeed been reported for hopping transport in molecularly doped polymers.[7] At present no theory is available to adequately include these complexities into hopping-time distribution functions more general than $\psi(t) \sim t^{-(1+\alpha)}$.

The different temperature behavior of the dispersion in the two polymers might be connected to subtle differences in their morphology. Unsubstituted PVK undergoes "crystallization" to produce folded chain paracrystals.[15] In a projection down the chain axis of these crystals the carbazole groups appear to have a regular trigonal symmetry about this axis. Although the interchain carbazole symmetry is lost in amorphous PVK, the intrachain carbazole symmetry and a considerable degree of chain parallelism are probably maintained.[12,16] On the other hand, for the bromine-substituted PVK the chain parallelism characteristic of unsubstituted PVK is not present and the polymer does not crystallize.[16,17] The random substitution of the bromine in either the 3 or 6 position (identical in the monomer but not in the polymer) can lead to random polarization of the carbazole group and random steric complications which override the van der Waals interactions that lead to chain parallelism in unbrominated PVK. This results in a considerably greater randomness in interchain carbazole-carbazole distances and orientations in 3Br-PVK and, furthermore, suggests a change in the intrachain carbazole symmetry and interactions. It is proposed that the different degree of ordering present in PVK and 3Br-PVK is reflected in the different temperature behavior of the dispersion of carrier propagation. Specifically, the increased randomness among the bromine-substituted carbazole groups might be the origin of the large and relatively temperature-independent dispersion of transient hole transport in this polymer.

In summary, PVK and 3Br-PVK provided model systems that exhibit dispersive transient hopping transport with features similar to hole transport in a-Se and a-$\mathrm{As_2Se_3}$, respectively. The different degree and temperature dependence of the dispersion in the two carbazole polymers is attributed to the different degrees of ordering in the amorphous phase. In some limited temperature range the Scher-Montroll CTRW based on $\psi(t) \sim t^{-(1+\alpha)}$ can explain the transport-time dispersion but more complicated hopping-time distribution functions are required to account for the data in the entire experimental temperature range. Finally, for the first time, nondispersive hopping transport in a random system has been reported.

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