Observation of the Transition from Adiabatic to Nonadiabatic Small Polaron Hopping in a Molecularly Doped Polymer

L. B. Schein, D. Glatz, and J. C. Scott
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

(Received 2 May 1990)

The transition from adiabatic to nonadiabatic small polaron hopping has unique characteristics among hopping theories; an activation energy in the mobility that changes from being monotonically increasing with the mean distance between hopping sites, ρ, to being independent of ρ, and, simultaneously, an Arrhenius prefactor that changes from being independent of ρ to exponentially decreasing with ρ. We have observed such a transition for the first time in the hole mobilities of the molecularly doped polymer, tri-p-tolylamine:polycarbonate.

PACS numbers: 72.20.Fr, 73.60.Hy

Theories of transport in amorphous systems can be classified by whether they consider energetic disorder to be of primary or secondary importance in determining the hopping rate. The former include the Scher-Montroll theory[1] of algebraic distributions of hopping times, Monte Carlo simulations of systems with both energetic and positional disorder,[2] and variable-range hopping theories.[3] Hopping theories that consider disorder to be of secondary importance include the small polaron theories of Emin[4] and Holstein[4] (in which the charge carrier induces a molecular distortion), phonon-assisted hopping,[5] and hopping over potential barriers between molecules. Establishing the applicability of a particular theory to an experimental system has been hampered by the similarity of the predictions of these theories (almost all hopping theories predict activated behavior) and the rarity of experimental systems in which ρ, the mean distance between hopping sites, can be varied.

One class of organic amorphous materials, molecularly doped polymers (MDP), has the special property that ρ can be varied by changing the concentration of the dopant. The experimental study of the behavior of the mobility μ as ρ is varied provides additional clues to the underlying hopping mechanism. Here we report the first observation of unique changes in the behavior of the hopping mobilities in an MDP as ρ is varied which are consistent with the predicted transition from adiabatic to nonadiabatic small polaron hopping.[4,6] Adiabatic small polaron hopping has been proposed for other amorphous materials, e.g., chalcogenide glasses,[7] which have activated mobilities and magnitudes of the mobilities consistent with small polaron theory. In contrast to MDP, ρ cannot be varied in these materials.

This present observation results from two recent advances, one involving an improved data-analysis technique[6] and one experimental.[6,8] The new technique allows deconvolution of mobility data into its electric field E, temperature T, and concentration-dependent factors. The experimental advance was the observation, after proper deconvolution, that mobilities in two MDP (see Fig. 1), (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4' diamine) TPD:polycarbonate[9] and (p-diethylaminobenzaldehyde-diphenyl hydrazone) DEH: polycarbonate[6,8] appeared consistent with adiabatic and nonadiabatic small polaron theory, respectively. The prediction made at the time was that if, for small ρ, a system were in the adiabatic regime, then by increasing ρ it should exhibit a transition to the nonadiabatic regime.[6,8] Here we report the realization of this prediction in the MDP, (tri-p-tolylamine) TTA:polycarbonate. This is the first experimental observation, to our knowledge, of the transition from adiabatic to nonadiabatic small polaron hopping and provides strong evidence for the applicability of small polaron theory to charge transport phenomena in molecularly doped polymers.

The technique suggested for deconvoluting mobility data (discussed in detail in Ref. 8) allows identification

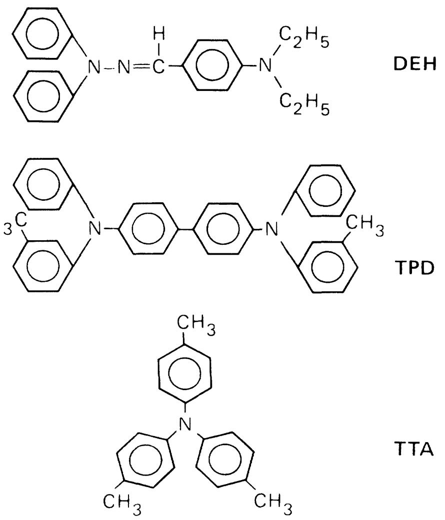

FIG. 1. The structure of the molecules discussed in text, TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4' diamine), DEH (p-diethylaminobenzaldehyde-diphenyl hydrazone), and TTA (tri-p-tolylamine).

of the dependence of the functions f_1 and Δ on ρ in the equation for the mobility in the limit of zero electric field,

$$\mu = a_0(T)\rho^2 \exp[f_1(\rho)]\exp[-\Delta(\rho)/kT]\,. \qquad (1)$$

In Eq. (1), the Arrhenius prefactor $\exp(f_1)$ conventionally is thought to describe the distance dependence of the electron transfer integral and is usually approximated as $f_1 = -2\rho/\rho_0$, where ρ_0 is a constant (≈ 1 Å) characterizing the exponential tail of the electronic wave function. $\Delta(\rho)$ is the activation energy required for hopping. At fixed ρ, $\Delta(\rho)$ is determined by extrapolating mobility data, $\mu(T,E)$, to zero electric field and linearly fitting $\ln\mu$ vs $1/T$, ignoring any algebraically weak temperature dependence of a_0. $a_0(T)\exp[f_1(\rho)]$ for each ρ is then determined from the $T=\infty$ intercept. This technique therefore allows the ρ dependence of Δ to be separated from the ρ dependence of f_1.

When this technique was applied to two MDP, DEH:polycarbonate[6,8] and TPD:polycarbonate,[9] a surprising result was uncovered.[6,8] It was found that, although these two systems are superficially similar, both molecules containing aniline moieties (see Fig. 1), the ρ dependence of Δ and f_1 were remarkably different. For TPD:polycarbonate, Δ increased monotonically with ρ while for DEH:polycarbonate, Δ was independent of ρ. For TPD:polycarbonate, f_1 was independent of ρ, while for DEH:polycarbonate, f_1 was linearly dependent on ρ, i.e., $f_1 = -2\rho/\rho_0$. Such data provide significant clues to the underlying hopping mechanism. While several authors have suggested mechanisms by which Δ may depend upon ρ (via a contribution to self-trapping from the electrostatic polarization energy of a localized hole[10,11]), these theories do not account for the simultaneous independence of f_1 on ρ. Further, despite the strikingly different behavior of Δ and f_1 on ρ in DEH:polycarbonate and TPD:polycarbonate, one would expect these systems to have the same underlying hopping mechanism. Therefore any theory which accounts for the data of one of these MDP should, by adjusting a parameter of the theory, be able to account for the data in the other MDP.

Small polaron theory can account for these seemingly disparate results.[6,8] Specifically, the mobility of a small polaron in the limit of zero electric field[4] can be expressed as

$$\mu = \frac{e\rho^2}{kT} P \frac{\omega}{2\pi} \exp\left[-\frac{\frac{1}{2}E_p - J}{kT}\right] \qquad (2)$$

or in terms of the parameters in (1),

$$a_0 \exp(f_1) = \frac{e}{kT} P \frac{\omega}{2\pi}\,, \qquad (3)$$

$$\Delta = \tfrac{1}{2}E_p - J\,, \qquad (4)$$

where e is the electronic charge, ω is a phonon frequency, J is the transfer integral, and E_p is the polaron binding energy. P represents the probability a charge carrier will hop once an energy coincidence between source and target sites occurs. The factors after P in Eq. (2) are the frequency of energy coincidences and $e\rho^2/kT$ converts a hop frequency into a mobility using the Einstein relation. Note that the activation energy is decreased by J because the energy levels are split by the overlap interactions during an energy coincidence.[4]

Small polaron theory predicts two hopping regimes.[4] The adiabatic regime is defined as $P=1$. In this regime, given an energy coincidence, the probability that a charge carrier will hop is unity. Consequently, f_1 does not depend on ρ. Such effects occur for large J, where J may be large enough to affect the value of the activation energy. Both predictions are evident in the data analysis of TPD:polycarbonate. The other, nonadiabatic, regime is defined as $P<1$. In this regime, given an energy coincidence, there is a probability less than 1 that the charge carrier will hop. Since $P \propto J^2 \propto \exp(-2\rho/\rho_0)$, $f_1 = -2\rho/\rho_0$. Since J is small, the activation energy is $E_p/2$, independent of ρ. This regime naturally accounts for the DEH:polycarbonate data. The small polaron description of transport in MDP leads to a prediction: If the small ρ regime is adiabatic, then at sufficiently large ρ there should be a transition to the nonadiabatic regime. We report the first observation of this transition in the MDP, TTA:polycarbonate whose structure is shown in Fig. 1.

Hole mobilities have been determined experimentally by standard time-of-flight measurements using a 9-mJ, 10-ns Molectron nitrogen laser. The laser light is strongly absorbed in the sample, which is typically 20 μm thick, creating a charge sheet which drifts across the sample in the applied electric field. At the lower TTA concentrations, thicker samples (≈ 40 μm) were used to ensure that the absorption length remained small com-

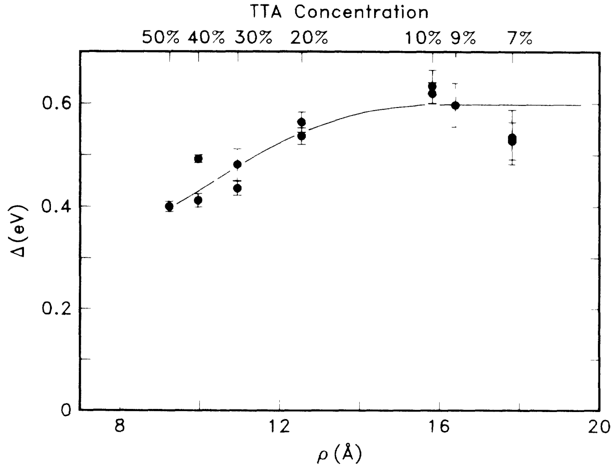

FIG. 2. The zero-electric-field activation energy plotted vs ρ. Note that it increases and then appears to saturate at about 15 Å.

pared to the sample thickness. Only measurements in which transit times could be obtained on linear current-time plots are reported; this is usually taken to indicate "nondispersive" transport. Several batches of TTA were used; all samples gave the same values of the mobility, indicating that the results are unaffected by any trace impurities. The data were taken up to electric fields of 100 V/μm over a temperature range from about 245 K to the glass transition temperature.

The results of the data analysis described above are shown in Figs. 2 and 3. The zero-field activation energy Δ increases as ρ increases and appears to saturate near $\rho = 15$ Å (Fig. 2). Moreover, f_1 is constant until about 15 Å after which it dramatically decreases with increasing ρ (Fig. 3). Hence, the regime $\rho < 15$ Å is consistent with the adiabatic small polaron theory and appears similar to observations made previously on TPD:polycarbonate and the regime $\rho > 15$ Å is consistent with the nonadiabatic small polaron theory and appears similar to observations made previously on DEH:polycarbonate. These results on TTA:polycarbonate represent the first time the transition from adiabatic to nonadiabatic small polaron hopping has been observed in a molecularly doped polymer and clearly confirm predictions made earlier based on identification of data on two different MDP with two limiting cases of polaron theory.

The transition occurs where P changes from 1 to less than 1, where $\hbar/J$ just equals the "duration" of an energy coincidence.[4] For DEH:polycarbonate, the transition is not seen up to the highest concentrations. For TPD:polycarbonate, it must occur $\rho > 16$ Å, beyond the range for which data are available and for TTA:polycarbonate it occurs at approximately 15 Å. We suggest that the reason for the transition occurring at these various values of ρ is associated with the different molecular shapes leading to different packing in polycarbonate and therefore different overlap of the π-electron systems.

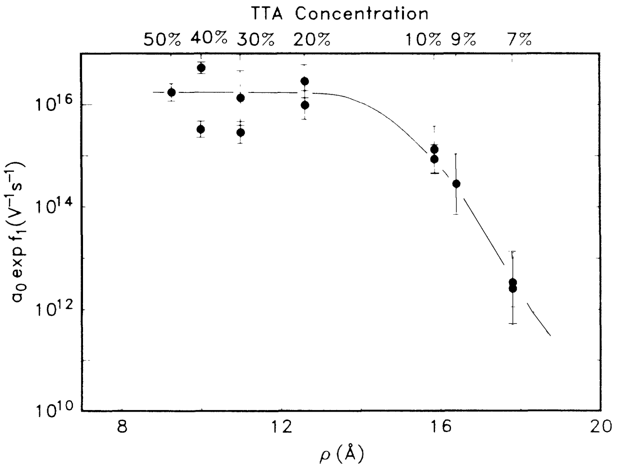

FIG. 3. The function $a_0\exp(f_1)$ plotted vs ρ. Note that it is constant and then begins to decrease at about 15 Å.

It is interesting that a theory which ignores disorder, which clearly is present in molecularly doped polymers both energetically and positionally, appears to describe data in this class of amorphous systems. It may be that disorder plays a secondary role because the energetic disorder is much less than the activation energy Δ. The disorder may be affecting the width of the distribution of arrival times which is much larger than one would expect from simple diffusion theory. Our conclusions depend upon an Arrhenius extrapolation to infinite temperature. The data fit an Arrhenius law $[\exp(-\Delta/kT)]$ well but they also fit the form $\exp[-(T_0/T)^2]$ advocated by Bässler[2] based on the assumption that Gaussian energetic disorder dominates the transport. The data do not cover a sufficient temperature range to distinguish whether T^{-1} or T^{-2} is a better description. However, the observation that analysis in terms of a simple Arrhenius activation results in a constant f_1 (shown in Fig. 3) requires explanation. For example, a constant f_1 could result from a coincidental cancellation of two effects (such as J and disorder changing simultaneously). Further, such a "coincidence" now has been observed in two different systems (TPD:polycarbonate and TTA:polycarbonate reported here), which appears unlikely to us.

The importance of polaronic effects is not unexpected in such conjugated molecular donors. Extensive theoretical[12] and experimental[13] studies have been made on similar compounds in order to determine the electron-phonon coupling constants. The results consistently show polaron binding energies on the order of 0.1–0.5 eV.

It is hoped that the present results will stimulate the extension of the available small polaron theory to multimode vibrational systems which should model molecularly doped polymers more realistically. Theoretical results relevant to several experimental observations would be particularly interesting. First, direct comparison of our data with Eq. (2) results in values of J (up to 0.25 eV) and $\hbar\omega$ (≈ 1 eV) which are larger than expected; it may be that an extension of the polaron theory to the complex molecules used in MDP will help resolve this issue. Second, the electric-field dependence of the mobility, discussed elsewhere,[2,14–16] remains to be explained. Third, a determination of whether the addition of disorder to small polaron theory can account for the distribution of arrival times and their dependence on temperature would be of interest.

In summary, we report the first observation in a molecularly doped polymer, TTA:polycarbonate, of a transition in behavior of the zero-field activation energy Δ and f_1 with ρ. Δ increases as ρ increases and appears to saturate near $\rho = 15$ Å; f_1 is constant until 15 Å after which it dramatically decreases with ρ. These results are consistent with the predicted transition from the adiabatic to nonadiabatic small polaron regime and hence provide strong evidence that the mechanism of charge transport in molecularly doped polymers is small polaron hopping.

We would like to acknowledge extensive discussions with Ralph Young and material characterization work done by N. Geoffrey Rule and John A. Sinicropi. The TTA was kindly suplied by the Eastman Kodak Company.

Note added.— Dr. P. Borsenberger of Eastman Kodak Company has independently made time-of-flight measurements on the same materials, and has obtained results in substantial agreement with those presented here. We wish to express our gratitude to Dr. Borsenberger for communicating these results prior to publication.

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