Computer simulation of photocurrent transients for charge transport in disordered organic materials containing traps

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ABSTRACT

We present results of computer simulations of the charge carrier mobility dependence on the electric field and trap concentration in disordered polar organic materials. Recently an unusual dependence of the charge carrier drift mobility in molecularly doped polymers on the concentration of traps has been reported. This dependence differs from the expected inverse proportionality that should be valid for trap-controlled transport. Using our results we argue that this dependence is caused by the existence of different regimes of charge carrier transport for layers with different trap concentrations, i.e. dispersive transport for small trap concentrations and nondispersive transport for high trap concentrations. Our results also show that the mobility, estimated from the time of intersection of the asymptom of plateau and trailing edge of photocurrent transient, is very sensitive to variation of transient shape and, in some cases, effectively masquerades real concentration and field dependence of the true mobility. Change of the shape with the change of electric field in trap-containing matrices distorts significantly the field dependence of the mobility, calculated by the intersection procedure, and even transforms the usual Poole-Frenkel dependence to the linear one.

Keywords: Charge carrier transport, disordered dipolar matrices

1. INTRODUCTION

Charge transport in molecularly doped polymers\textsuperscript{1,2} (MDPs) is of significant interest because of its importance in xerographic process where MDPs serve as transport layers in dual-layers photoreceptors. Knowledge of transport properties of these materials is an essential part of technological know-how for design of high-speed laser printers and copiers. At the same time, MDPs are members of the broader class of organic disordered materials with common transport features. Other examples of materials of this class are low molecular weight organic glasses\textsuperscript{3,4} and certain polyconjugated polymers.\textsuperscript{5,6} Recent efforts\textsuperscript{7-14} established a new basis for understanding transport properties of these materials. It has been found that the most fundamental property of charge transport, the so-called Poole-Frenkel (PF) mobility field dependence\textsuperscript{1,2,5}

$$\mu \propto \exp \left( \gamma \sqrt{E} \right),$$

arises naturally in disordered systems where carrier's interaction with randomly oriented and situated molecules possessing permanent dipole moments provides a significant contribution $U_d$ to the total site energy. The most important property of dipolar medium is the strong spatial correlation in the distribution of energies of transport sites that can be characterized by slow decay of the corresponding correlation function

$$C(r) = \langle U_d(r)U_d(0) \rangle \propto \sigma^2 \frac{a}{r},$$

where $\sigma^2 = \langle U_d^2 \rangle$, and $a$ is a minimal charge-dipole separation.\textsuperscript{7,9} In recent studies\textsuperscript{7,9,10,14} it has been shown that the model of dipolar glass gives a good explanation of main transport properties of disordered organic materials. Extensive computer simulations suggest that the overall mobility dependence on electric field and temperature in correlated (dipolar) media has the form\textsuperscript{14}

$$\mu = \mu_0 \exp \left[ - \left( \frac{3\sigma}{5} \right)^2 + C_0 \left( \frac{3\sigma}{5} - \Gamma \right) \sqrt{\frac{eaE}{\sigma}} \right],$$

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Part of the SPIE Conference on Xerographic Photoreceptors V
Denver, Colorado • July 1999
SPIE Vol. 3799 • 0277-786X/99/$10.00
where \( \tilde{\sigma} = \sigma/kT \), \( C_0 = 0.78 \), and parameter \( \Gamma \) equals to 2 for dipolar glass with no positional disorder but should be greater for spatially disordered system.

Analytic solution of the 1D version of dipolar model suggests\(^9\) that the mobility field dependence in a medium having an energy-energy correlation function of the kind \( C(r) \propto 1/r^p \) has the form \( \ln \mu \propto E^{p/(p+1)} \); thus the necessary and sufficient condition for realization of PF mobility dependence is \( p = 1 \). Until now the only model that gives exactly this kind of asymptotic behavior for \( C(r) \) is the model of dipolar glass. Again, both the analytic solution of 1D model\(^9\) and results of extensive computer simulation\(^14\) suggest that in a dipolar glass the PF dependence is a direct consequence of this particular asymptotic decay of correlation function (Eq. 2), and not the property of the particular form of hopping rate, as it is in the old Gaussian disorder model.\(^15\)

The only important assumption of the dipolar model is the conjecture that a large class of disordered organic materials may be described as dipolar glasses. Until recently one of the most important arguments against this model was a frequent observation of pretty good PF dependence in nonpolar materials.\(^16\) A careful analysis reveals, however, that for nonpolar materials there is no credible evidence of observation of the PF dependence in a really broad field range, compared, for example, with the range from \( 8 \times 10^5 \) to \( 2 \times 10^6 \) V/cm, examined in the paper of Schein et al.\(^1\)

A typical field range in question spans less than one order of magnitude (and, quite frequently, field strength varies no more than 4-6 times, see Ref. 16 for low temperature data). For this rather narrow field range a quasi-PF field dependence, such as, for example, \( \ln \mu \propto E^n \) with \( n \) not significantly greater than 1/2, may successfully mimic a true PF dependence. A recently proposed model of a quadrupolar glass, which gives \( C(r) \propto 1/r^3 \) and, hence, \( \ln \mu \propto E^{3/4} \), presents a probable explanation of this striking disagreement.\(^13\) The importance of the quadrupolar contribution to the resulting mobility field dependence arises from the fact that a great majority of organic compounds, even nonpolar ones, have rather large quadrupole moments. Contributions from dispersive transport, usually unavoidable in experiments, brings the quasi-PF mobility dependence even more close to the true PF one.\(^13\)

 Pretending to be the true model of charge transport in polar organic materials, the dipolar model should describe as many features of the transport as possible. One particular important area of exploration is trap-controlled transport in dipolar materials. Indeed, it is well known that, in a typical case, the transport layer contains impurities serving as traps and, quite frequently, significantly affecting the transport properties of the material. One striking example of the importance of traps was recently discussed by Borsenberger et al.\(^17\) In this particular case a much more careful method of transport layer preparation (isolation of components from the exposure to light and air, thus presumably decreasing the amount of impurities created in the preparation process) significantly changes the observable dependence of the transport activation energy on transport site concentration.

Taking into account the significance of trap effects on charge transport, a question arises as to what extent a general picture of the charge transport in a smooth correlated energy landscape survives under the action of traps, which are the source of totally uncorrelated disorder. Our previous results\(^13\) indicate that the PF dependence in moderate fields remains essentially the same in the presence of traps (apart from the trivial vertical displacement of the curve downwards) for any trap concentration and depth, while in stronger fields a new dependence develops, namely the linear one

\[
\ln \mu \propto e aE/kT, \tag{4}
\]

where \( a \) is close to the mean distance between transport sites.

In recent papers Vertas and Juhas,\(^18\) Wolf et al.,\(^19\) and Lin et al.\(^20\) studied the transport of holes in doubly doped polymer layers. Molecules of one dopant, added in small concentration, and possessing significantly lower ionization potential, served as traps for charge carriers. In these studies it was found that, for shallow traps, the PF dependence remains mainly untouched,\(^18,19\) while for deep traps a linear dependence (Eq. 4) was observed in the whole field range.\(^18\) Resolution of this discrepancy is one of the aims of the present paper.

The most puzzling experimental result, first observed in Ref. 18, and later confirmed in Ref. 20, is the unusual dependence of the mobility on trap concentration \( c \)

\[
\mu \propto 1/c^n, \tag{5}
\]

with \( n > 1 \) instead of expected dependence with \( n = 1 \) for trap-controlled transport. This result does not agree with the theoretical dependence found in Ref. 13, where \( n = 1 \). Resolution of this disagreement is the main purpose of this study.
Figure 1. Photocurrent transients for transport layers with different fraction of sites, occupied by traps (indicated on plots); $\sigma/kT = 3.83$, $e\Delta E/\sigma = 0.44$, $\Delta/kT = 10$ and transport layer thickness is 20,000 lattice planes ($\tau$ is the Miller–Abrahams time scale). If $T = 298$ K and $a = 10$ Å, then $\sigma = 0.098$ eV, $\Delta = 0.26$ eV, and $E = 4.3 \times 10^5$ V/cm.
In Ref. 18 it was found that for two particular kinds of traps \( n \approx 1.33 \), while in Ref. 20 several different traps were investigated and it was found that \( n \) is a monotonously increasing function of trap depth with \( n > 1 \) for deep traps (\( \Delta > 0.22 \) eV, here \( \Delta \) is a trap depth). Note, that Eq. 5 with \( n = 1 \) is a common feature of trap-controlled transport regime for any reasonable model of hopping charge transport and small trap concentration (when we can neglect the direct hops between traps). Indeed, this dependence means that at small concentration traps act independently and do not alter notably transport properties of the surrounding matrix. Thus, the solution of concentration puzzle seems to be of significant interest for general understanding of the properties of hopping transport.

2. UNUSUAL CONCENTRATION DEPENDENCE AS A RESULT OF DISPERSIVE EFFECTS

The first clue for the solution of concentration puzzle is the obvious difference in characteristics of photocurrent transients for different concentrations of traps. Namely, at room temperature, transients for the trap-free matrix usually have nondispersive shape: a short initial spike, then a well-defined plateau, and then an abrupt decrease (see Fig. 1 for \( c = 0 \)). Such a shape indicates that a majority of carriers move with approximately identical velocities. After the addition of a small quantity of traps, the photocurrent transients attain dispersive features (in some cases the transient becomes so dispersive that even determination of the drift time in a double linear plot is not possible). For greater trap concentrations the transients again become nondispersive, with much lower mobility (in comparison to the trap-free case). Finally, for a significant concentration of traps, the mobility increases because direct hopping between traps becomes possible: this regime is of no interest for the trap-related problem. The transition from nondispersive trap-free transport to nondispersive trap-controlled transport is shown in Fig. 1. This figure is the result of computer simulation but demonstrates the same type of behavior as the experimental data in Ref. 18.

Hence, in a typical experimental situation, for a thin transport layer, the mobility for different trap concentrations is measured for very different transport regimes: dispersive transport for small trap concentrations and nondispersive transport for high trap concentrations (see, for example, Fig. 3 in Ref. 18). For the same value of temperature and electric field, the dispersive mobility is greater than the nondispersive equilibrium mobility (suppose, we can measure both of them, for example, in layers of different thickness). Dispersive mobility is greater because this is the mobility of hot carriers which did not undergo full energy relaxation. Hence, the true nondispersive mobility for small trap concentration (measured in very thick layers) should be smaller than the mobility measured in Refs. 18,20. Figure 2 demonstrates that this modification should lead to the decrease of \( n \); it is possible that in such a case \( n = 1 \), as it should be for trap-controlled transport.

3. COMPUTER SIMULATION

To test this explanation we carried out a computer simulation of trap-affected charge carrier transport in disordered organic materials of dipolar origin. For transport simulations we used a simple cubic lattice of \( 50 \times 50 \times 50 \) sites with lattice parameter \( a \), occupied by randomly oriented dipoles with dipole moment \( p \), from which an extended transport layer is formed by periodic continuation. The energy of a carrier at a given site is then the sum (calculated using the Ewald method\(^{21}\)) of its interaction with dipoles at all sites except its own. For this particular model of dipolar glass\(^{22,23}\)

\[
\sigma = 2.35 \varepsilon p / ca^2, \tag{6}
\]

where \( \varepsilon \) is the dielectric constant. For a fraction \( c \) of all transport sites a constant value \( \Delta \) was subtracted from the site energy, thus modeling traps.

To determine the photocurrent transients, we performed Monte Carlo (MC) simulations using Miller-Abrahams hopping rates that fall off with distance as \( \exp(-2ar) \). We took \( 2a = 10 \), as in Ref. 15. For each particular time interval the current was calculated as a quantity, proportional to the instantaneous velocity of charge carrier. To save computation time, for each transport site only hops to all other transport sites which occur with probability more or equal to \( 10^{-5} \) of the maximum probability for this particular site were taken into account.

We calculated mobility by three different methods: 1) \( \mu_v = \langle v \rangle / E = L / (1 / t_{MC}) / E \), where \( \langle v \rangle \) is the average velocity of a carrier, \( L \) is the layer thickness, and \( t_{MC} \) is the time that a carrier needs to reach the opposite electrode; unfortunately, one cannot calculate \( \mu_v \) directly from the temporal dependence of the photocurrent, hence, this method, being the superior one from theoretical point of view, cannot be directly applied to analysis of experimental data (see, however, Eq. 7); 2) \( \mu_i = L / t_i E \), where \( t_i \) is the time of intersection of asymptotes to the plateau and
Figure 2. Typical experimental mobility dependence on the trap concentration (diamonds) and anticipated dependence for nondispersive transport in the whole concentration range (broken line).

trailing edge of the transient; 3) \( \mu_{1/2} = L/t_{1/2}E \), where \( t_{1/2} \) is the time for photocurrent to decay to the half of its plateau value (see Fig. 3). The second method is the method of choice for most experimental papers.

4. RESULTS AND DISCUSSION

Figure 4 demonstrates the mobility concentration dependence for different thickness of a transport layer and clearly confirms the suggested explanation for the unusual mobility concentration dependence: the thicker the transport layer (and, hence, the less is the contribution of dispersive transport), the less is the value of \( n \) in Eq. 5. For thick layers this value is very close to 1 (see Fig. 5). In other words, transport in thin layers is not so sensitive to small concentration of traps because the majority of carriers avoids traps. For this reason the mobility in thin layers does not drop significantly from the corresponding value for the trap-free matrix. For high trap concentrations a major part of carriers undergoes multiple trapping; even in thin layers, transport is essentially nondispersive, and the trap-induced decrease of the mobility does not differ significantly from the correspondent decrease in thick layers. Hence, the difference in mobility values for small and high trap concentrations is greater for thin layers (dispersive transport). This effect inevitably leads to the greater value of \( n \) for the dispersive transport in thin layers. Hence we beg to differ with the statement, raised in Ref. 18, that the observed unusual concentration dependence “could only be explained by a new theoretical approach”; increase of \( n \) with increase of \( \Delta \), observed in Ref. 20, is quite understandable, because increase of \( \Delta \) leads to increase of the dispersive component of charge transport.

Our simulation raises a very important question concerning interpretations of experimental data. In previous discussions we used mobility \( \mu_v \), calculated from the average velocity of charge carriers. This mobility has a clear advantage over \( \mu_i \) and \( \mu_{1/2} \), because it literally matches a usual theoretical definition. However, because it is impossible to calculate \( \mu_v \) directly from experimental data, discussion of experimental results values of \( \mu_i \) (mainly) and \( \mu_{1/2} \) (very rarely) are used. Our results show that the strong preference for the use of \( \mu_i \) instead of \( \mu_{1/2} \) leads, in some cases, to wrong conclusions. The danger of use of \( \mu_i \) is clearly demonstrated in Fig. 6, because even for the very thick transport layer (one million planes!) value of \( n \) for \( \mu_i \) differs significantly from 1. Figure 6 indicates that calculation of mobility from \( t_{1/2} \) seems to be a more credible procedure; it should be used instead of the extremely
unreliable procedure that employs \( t_i \). The overwhelming use of the intersection procedure undermines credibility of discussion of many experimental results.

Additional confirmation of our last statement may also be found in Ref. 18. We have already mentioned that, for deep traps, the mobility field dependence observed in this paper has a linear form (Eq. 4) in the whole field range, in striking contrast with the theoretical prediction. This disagreement can be explained by the same phenomenon: a different contribution of dispersive transport for different field strengths (it is worth noting that for shallow traps with less dispersive transport the usual PF dependence has been observed\(^\text{18}\)). If this explanation is true, then we should expect: 1) transformation of the shape of the photocurrent transients with the variation of electric field and 2) a notable difference in the functional forms of \( \mu_i(E) \) and \( \mu_o(E) \) dependences. Figures 7 and 8 confirm these predictions. Again, mobility, calculated from \( t_{1/2} \) is much more close to the mobility, calculated from the average MC velocity. The difference between \( \mu_i \) and \( \mu_o \) (and \( \mu_{1/2} \)) is most significant for small fields, and is so significant that the functional dependence of \( \mu_i \) on \( E \) (linear) is totally different from the functional dependence of \( \mu_o \) and \( \mu_{1/2} \) (usual PF dependence). Again, as in the case of concentration dependence, use of \( \mu_i \) distorts the true mobility field dependence.

The ultimate reason for this distortion is very simple: by definition, \( \mu_i \) is sensitive to the particular shape of transient, and overestimates the contribution of fast carriers. Hence, if in some parameter range (be it electric field, concentration of traps, or something else) the shape of transient varies significantly, then the use of \( \mu_i \) for revelation of functional dependence of carrier mobility on this particular parameter is under great suspicion. At last we would like to note that the best way to calculate the mobility (from the point of view of its closeness to the usual definition as the mean carrier velocity over the electric field strength) is to calculate it by the formula

\[
\mu = \frac{\langle v \rangle}{E} \approx \frac{I_p L}{Q E} = \frac{I_p L}{E \int_0^\infty dt I(t)},
\]

(7)

where \( I_p \) is a current at the plateau and \( Q \) is the total charge flowed through a sample. This formula can be used only in the case when a real plateau with an approximately constant current \( I(t) \approx I_p = e \rho \langle v \rangle S \) is detected in the
Figure 6. Mobility dependence on the trap concentration for $\sigma/kT = 3.83$, $eaE/\sigma = 0.44$, $\Delta/kT = 10$, and $L = 1,000,000$ lattice planes for different methods of mobility calculation: $\mu_e$ - diamonds ($n = 1.05$), $\mu_{1/2}$ - squares ($n = 1.13$), and $\mu_i$ - triangles ($n = 1.28$).

Figure 7. Photocurrent transients for $\sigma/kT = 3.83$, $\Delta/kT = 10$, $c = 0.01$, $L = 40,000$, and two values of $eaE/\sigma$: 0.021 (thin line) and 1.70 (thick line), correspondingly, with time axis rescaled to make values of $t_{1/2}$ equal for both transients. Note the different shapes of transients.

Figure 8. Mobility dependence on the electric field for $\sigma/kT = 3.83$, $\Delta/kT = 10$, $c = 0.01$, and $L = 40,000$ lattice planes for different methods of mobility calculation: $\mu_e$ - diamonds, $\mu_{1/2}$ - triangles, and $\mu_i$ - squares.
experiment (here \( \rho \) is the density of carriers and \( S \) is the sample area), and one can measure the photocurrent for a long time interval, to be sure that the integral in Eq. 7 is calculated with sufficient accuracy.

5. CONCLUSIONS

The dependence of carrier drift mobility in disordered dipolar materials on the concentration of traps has been studied using computer simulation. We have found that unusual concentration dependences, observed recently,\(^{18,20} \) are the result of a transition from dispersive to nondispersive charge transport with increase of trap concentration. Experimental tests of this result should be of the same nature as the computer simulation itself - a measurement of carrier mobility for small trap concentration in thick layers, much thicker than previously investigated; such measurement is possible\(^{24} \) for the transport systems studied in Ref. 20.

We showed that in some situations the mobility, calculated in a usual way, by the time of intersection of two asymptotes - to the plateau region and to the trailing edge of the transient - plays a misleading role in the revelation of the mobility dependence on the electric field and trap concentration. The best way to calculate the nondispersive mobility is to use Eq. 7. If it is not possible for some reason, then the mobility, calculated by the time for photocurrent to decay to the half of its plateau value, should be used for discussion of experimental results.

ACKNOWLEDGMENTS

This research, conducted in part at the Albuquerque High Performance Computing Center and the Maui High Performance Computing Center, was partially sponsored by the US Air Force Research Laboratory, Air Force Material Command, USAF, under cooperative agreement F29601-93-2-0001, and also by the International Science and Technology Center grant 872-98, Russian Fund for Basic Research grant 99-03-32111. Discussions with P.E. Parris and D. Emin are gratefully acknowledged.

REFERENCES

24. P.M. Borsenberger, private communication.