

Modeling of electronic transport in molecular doped polymers by the time-of-flight method

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Received 3 August 2004, accepted 20 September 2004

Abstract

We present here a review of electrical transport models in Molecularly Doped Polymer (MDP) materials used for photocopiers and laser printers. The common method of electronic transport evaluation in these materials employs measurements of transient photocurrent by the time-of-flight (TOF) technique. TOF experiments use mainly the mobility concept to elucidate the mechanisms of electronic transport in MDP. However, additional experimental parameters are needed to account satisfactorily for the temperature and electric field activated complex transport phenomena observed in these materials. In particular, the spatial and energy dispersive experimental details have been left out in most experimental works while measuring the transient electrical conductivity in MDP. Additional information regarding the velocity distribution of the spreading charge packets and trapping models are detailed in this work for achieving a better understanding of the electronic charge transport in MDP. This review brings together the current theories extended for the electrical transport in these materials.

PACS: 72.10.Bg, 72.20.-i , 72.80.Ng, 72.80.-r, 72.90.+y

1 Introduction

During the last two decades charge transport in Molecularly Doped Polymers (MDPs), or the so-called disordered organic systems, has become a topic of intensive research due to their use as photoconductors [1–3], photo-refractive devices, organic light-emitting diodes (OLEDs) [4–10] and synapse bond devices [11–13].

MDP consist of charge transport molecules dispersed in a host polymer matrix. All above-mentioned applications of these devices involve electrical carrier transport. In addition to their practical significance, MDP are also a good choice for studying basic mechanisms of charge transport in molecular solids, as all the relevant variables, including temperature, electric field, and the distance between hopping sites, easily can be varied in them.

Carrier transport can be evaluated by various means but the commonly used method is the Time-Of-Flight (TOF) technique [1–3, 14, 15]. In this technique, the induced transient current is measured when a charge carrier packet moves in a thin sample. TOF experiments in organic materials [6, 16–18] and other insulating systems [1, 19] give the kinetics of transient current with an initial fast drop to a near plateau level shown in Fig. 1a for a specific MDP system - pyrazoline compound in polycarbonate, DEASP:PC (Dyethyl-Aminostyryl-Diethylphenil-Pyrazoline in PC).

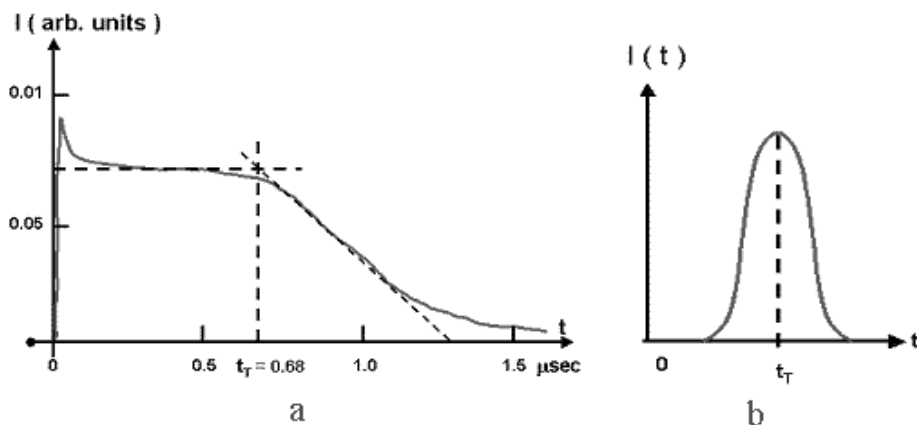


Figure 1: TOF transient current curves for: (a) DEASP 50%, $L = 8.3\mu\text{m}$, $V_0 = 300(\text{V})$, $T = 285\text{K}$, $t_{tr} = 68\mu\text{sec}$ [20]; (b) Typical TOF transient current for semiconductors.

When the transport charge is collected at the receiving electrode, there is another drop in the current amplitude. Possible suggested models various spatial dispersion mechanisms involved in charge transport, such as diffusion, trapping, Coulombic spread and detrapping. The current shape thus can be quite intricate and depends also strongly on parameters such as device thickness, temperature, dopant level and electric field intensity [1, 6].

The shape of the transient currents in MDP differs significantly from that in semiconductor materials, shown in Fig 1b, thus the well-developed theory of charge transport in semiconductor crystalline materials is not useful for describing charge transport in MDP [2, 21]. Many investigators identify the above mentioned TOF signals characteristics with the so-called ‘nondispersive’ charge transport [4, 17]. In this case the TOF current transients inflection point is taken by most investigators as the carrier transit time, from which the bulk drift mobility, μ , is calculated. The time $t_{1/2}$, where the transient current falls to half its maximum value, is also used sometimes, e.g., [4, 22]. Mobility is taken by most investigators as the sole important electrical characteristic of charge transport layers in MDP. However, since electrical carrier motion is, generally, a complex function of many physical factors, several types of mobility are defined, such as microscopic mobility μ and effective mobility μ_{eff} [23]. As the mobility of charge carriers in polymeric systems is typically several orders of magnitude lower than in crystalline systems one has to understand how disorder reduces the effective mobility [24]. The interpretation of data differs in the details from system to system, but is usually based on the assumption that the transport has a “hopping” nature and dispersive in the sense that the drift velocity is combined with the velocity of charge packet spread through hopping sites which are distributed homogeneously in the material [2, 23].

Numerical investigations of hopping transport in the disordered matrix were undertaken by Bäessler [6, 25], Gartstein and Conwell [26], Dunlap *et al.* [27], Novikov *et al.* [28], and Fishchuk and coworkers [29]. Important simulations of hopping in energetically disordered lattices with a Gaussian Density of States (DOS) denoted as the Gaussian Disorder Model (GDM) were performed by Bäessler [6, 25]. Gartstein and Conwell [26] suggested that the spatial correlation of the energies of transport sites in disordered media has to be taken into account also to describe properly the field dependence of mobility over a broad electric field range. Extensive computer simulations by Dunlap and coworkers [27], and Novikov *et al.* [28], resulted in an amended version of the formalism, which provided a good explanation of the experimental analysis. The latter was also supported by an analytic effective-medium theory recently developed by Fishchuk and coworkers [29],

which demonstrated that the disorder formalism can also account for peculiarities of charge transport in weakly disordered organic systems, provided one uses the correct expression for the jump rates.

One of the limitations of the disorder formalism is, however, that it does not address carrier transport in the presence of traps. This has led to the recent interest in trapping effects [29–33]. Traps in disordered media are extrinsic, localized states that differ from the majority carrier hopping states in that they require substantially larger input energy to release the charge carriers back to the intrinsic DOS. For instance, a hole or electron propagating through a material may be affected by trapping on a molecule of another type of material provided the latter has a lower ionization potential or a higher electron affinity. The problem of trap-controlled transport is also recognized as being very important in applications of new organic materials used for electronic devices. For example, since electronic transport in π -conjugated polymers is often trap affected, charge-carrier transport controlled by deep trapping becomes important in photorefractive organic systems where moderately deep traps play an essential role.

In practice TOF experiments in MDP exhibit either a so-called spatially ‘dispersive’ TOF transient characteristic with an almost unrecognizable plateau region, or with a slope or inclination in the plateau region of Fig. 1a.

Typically, the mobility μ is derived from the time t_T defined by the intersection of the asymptotes to the plateau and tail of the photocurrent transients [1–3], see Fig. 1a. Usually, the tail of the current does not decrease linearly. Hence the velocity obtained from the measured transit time t_T and the sample thickness is not the mean velocity of the moving charge packet.

To overcome the difficulty in the explanation of these experimental features in charge transport properties of various polymer materials, investigations were undertaken on charge transport process in the last two decades using different courses based on different points of view. Some authors attempted to analyze TOF-transients using electrostatics and electrodynamics concepts [14, 18, 21, 32–34] while others used the physical models of disorder in evaluating solids charge carrier distribution and transport [6, 9, 25, 27, 35–37].

2 Mobility investigations

The major result of experimental studies in organic solid thin films was the observation of the exponential dependence of the mobility μ [2, 3] on the

external applied electric field and temperature, phenomenologically represented by the expression given by Gill [38] :

$$\mu(T, E, \rho) = \mu_0 \exp \left[- \left(\Delta_0 - \beta \sqrt{E} \right) \left(\frac{1}{kT} - \frac{1}{kT_0} \right) \right] \quad (1)$$

where $\mu(T, E, \rho)$ is the drift mobility as a function of temperature T , electric field E , and dopant intramolecular distance ρ . k is the Boltzmann's constant, Δ_0 the zero electric field activation energy and μ_0 , β and T_0 are fitting constants discussed in detail in [20]. The values of the parameters T_0 , Δ_0 and β are determined from TOF measurements and depend on the material, but the \sqrt{E} dependence and the shifted Arrhenius temperature activated behavior are universal.

The dependence $\mu \propto \exp \sqrt{E}$ suggests the Poole-Frenkel effect, i.e., the lowering of the Coulomb barrier by the applied electric field [16] or Schottky barrier lowering due to image forces.

For a long time this empirical expression has been subjected to intense theoretical and experimental investigations [39], to explain the peculiar dependencies embodied in equation (1). Pfister [40] used an empirical expression identical to (1) with $\beta \sqrt{E_0} = \Delta_0$, which allowed an alternative method of obtaining Δ_0 , i.e., extrapolating $\ln \mu$ vs \sqrt{E} (with T as a parameter) to a field $\sqrt{E_0}$ at which the mobility temperature dependence vanishes.

The intersection of the lines on the Arrhenius plot of mobility measurements for typical MDP, shown in Fig. 2, gives a temperature T_0 at which the E-dependence vanishes (the so-called compensation temperature) and was observed experimentally by Peled and Schein [41].

The physical origin of the compensation temperature T_0 remains unclear to date although some explanations have been proposed by Peled and Schein [42]. An attempt to relate the microscopic origin of the compensation temperature to the competition between positional or orientational disorder and energetic disorder has been given by Soos *et al.* [43]. As shown in Fig. 2, the temperature T_0 has been observed to occur experimentally [16]. For data points with $T > T_0$, the slope of the mobility - field strength dependence is negative:

$$\frac{\partial \mu}{\partial E} < 0 \quad (2)$$

while for $T < T_0$ it is positive:

$$\frac{\partial \mu}{\partial E} > 0 \quad (3)$$

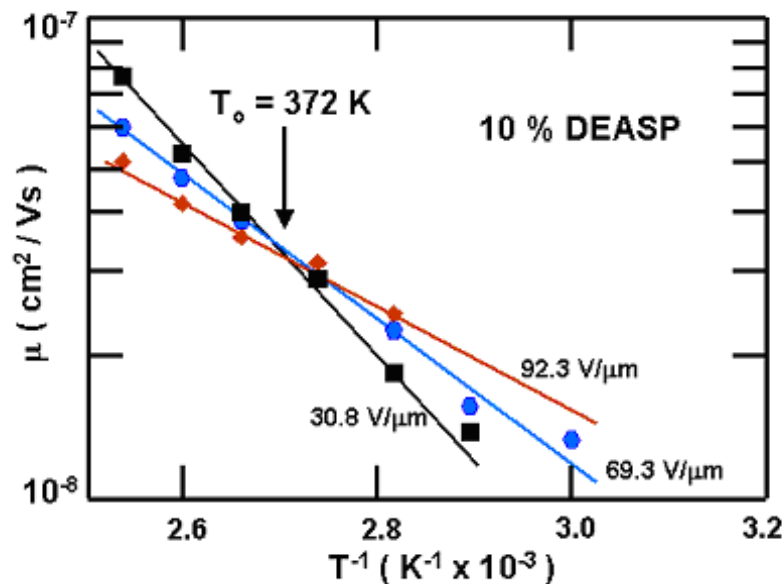


Figure 2: Mobility versus T^{-1} plot. Another method of obtaining T_0 is to plot the mobility versus electric field with T^{-1} as a parameter and obtain the temperature at which the field dependence vanishes. The value obtained in this plot is $T_0 = 372$ °K. (Plot from [41])

The latter is the more commonly observed behavior, in which the electric field lowers the barrier of escaping from the Coulomb potential [6, 16, 44]. To probe the physical significance of the field dependence of mobility, Schein and coworkers [16] have obtained data over the widest electric field range yet reported, from 0.82 to 206 V/ μm .

Most workers in this field agree that charge transport in MDP occurs by 'hopping'. The charge carrier is viewed as highly localized, hopping among dopant molecules, with the polymer matrix serving mainly as an inert spacer. In this model, the physical effect of the electric field is usually thought to bring energy levels into closer coincidence, thereby reducing hopping energy barriers. This model leads to the intuitive prediction that larger electric fields should increase the mobility. However, the experiments [41] in which hole mobilities were observed for the first time to decrease with increasing electric fields, suggest that this picture may be incomplete.

Schein and coworkers [16] made the following conclusions. Over the

entire range, the data are consistent with a field dependence of the form $\exp \sqrt{E}$ and no other function suggested in the literature is consistent with the data. While such a functional dependence is predicted by the Poole-Frenkel theory, Schein and coworkers [16] showed an order of magnitude agreement with this theory, but several objections to the applicability of this theory to the data were raised. As many authors have pointed out, it is difficult to assume that the space charge created by such a concentration of Coulomb centers can exist in MDP films and be undetected. Schein and coworkers [16] have pointed out also that the distance to the top of the potential barrier which they estimated in the range $r_p \approx 43 \div 430 \text{ \AA}$ for typical fields in the range $E \approx 10 \div 100 \text{ V}/\mu\text{m}$ is much larger than the calculated distance between the molecules 10 \AA for 50% DEH: polycarbonate. Therefore, the hole should complete its hop in a much shorter distance than the distance to the peak of the potential barrier determined by the Coulomb potential and the applied electric field [16]. Finally, the Poole-Frenkel effect does not explain the temperature-independent, field-dependent term at T_0 , whose physical origin remains unclear.

3 Dispersive and nondispersive TOF transients

The nondispersive TOF transient current form with a distinct plateau was related to the bulk mobility, while the dispersive tail is understood by most investigators as the label for identifying specific mechanisms in TOF current transients such as carriers' dispersion. Several theories have been developed to analyze the microscopic origin of carrier dispersion [22]. The first was the continuous - time random walk (CTRW) theory developed by Scher and Montroll [45] which describes the process in statistical terms and therefore does not specify the underlying physical mechanism. The CTRW theory is based on a non-Markovian transport process. According to the theory, the carrier migration is a time-dependent random walk controlled by a slowly varying broad distribution of hopping times. Featureless dispersive non-Gaussian transients and an anomalous thickness dependence of drift mobility were predicted and indeed observed in amorphous As_2Se_3 [46] and in triphenylamine molecularly dispersed in polycarbonate [40]. The thickness dependence of the mobility is generally interpreted as an anomalous dispersion of the charge carrier sheet.

Amorphous organic charge-transporting solids are typically characterized by a very weak van der Waals type of bonding between molecules resulting in very narrow energy bands for which the common band the-

ories of charge transport are not adequate. Instead, it has been widely recognized that charge transport in amorphous organic solids is a hopping process, which involves electric field driven charge exchange between neighboring molecules. The charge hopping probability is governed by the energy matrix of the amorphous solid which is a sensitive function of the intermolecular distance and the mutual molecular orientation [22]. The fluctuation of the molecular site energies is commonly referred to as ‘diagonal disorder’ and the fluctuation of the intermolecular distances is referred to be the ‘off-diagonal elements’ of the energy matrix. Several computer simulation studies have been carried out in an effort to analyze separately the effect of the off-diagonal and diagonal disorder of charge dispersion. This was done by simulation of hopping either among a spatially random array of isoenergetic sites [47] or as a cubic lattice of a Gaussian distribution of hopping site energies with a 0.1 eV width [25]. Both studies predicted that anomalous dispersive transport could be observed only in the early stages of the transient, typically within the first few percent of the overall transit time. This early dispersive region was determined to be the consequence of the dynamic equilibration of the carriers with the environment following the instantaneous injection of a sheet of carriers into the bulk of the material. After this equilibration stage, the simulated current trace becomes less dispersive, i.e. with features of a plateau and a long tail. Pfister and Scher [46] conclude that such a feature also be referred to as dispersive or non-dispersive, depending on the slope of the plateau and the length of the tail.

4 The effective temperature T_{eff}

The effective temperature T_{eff} defined by the relationship $T_{eff}^{-1} = T^{-1} - T_0^{-1}$ from Eq. (1) has been defined to cast experimental results symmetrically with respect to field and temperature [38, 40]. Like T_0 , this experimental temperature, T_{eff} , appears to be a new transport system parameter, with no obvious physical interpretation. It has been suggested [24, 40] that the effective temperature originates from a temperature dependent dispersion parameter indicating a spread of the activation energy of the hopping carriers, that is, diagonal disorder for an exponential distribution of trap-release energies $N(\varepsilon) \propto \exp(-\alpha\varepsilon/kT)$, $T_0 = \alpha^{-1}T$ [40]. α is the measure of the dispersion for the ideal case of non-Gaussian transport which occurs for transit times t_T of the order of individual hopping times, when the dispersion of the carrier packet is caused by fluctuations of the bulk mobility. In

this case, the TOF current is approximated to be independent of the actual source of dispersion [40, 45] and given by:

$$I(t) \propto \begin{cases} t^{-(1-\alpha)}, & t < t_T \\ t^{-(1+\alpha)}, & t > t_T \end{cases} ; \quad 0 < \alpha < 1, \quad (4)$$

For temperature-independent fluctuations of the hopping distance: $\alpha \cong \rho_0/\rho \{\ln [L/l(E)]\}^{2/3}$ where $2\rho_0$ is the Bohr radius of the charge localization, L is the thickness of the layer and $l(E)$ is the mean displacement from the illuminated surface. Also $t_T \propto (L/l(E))^{1/\alpha} \exp(\Delta/kT)$. However, while the temperature dependence of α can rationalize the results in the non-Gaussian regime, when the mobility measured by TOF depends on the sample thickness, the activation energy which results from a typical Gaussian distribution of width for polymers, is much smaller than experimentally observed. Also, the time range where non-Gaussian transport prevails is much too short. Bässler [6] showed that the phenomenologically defined compensation temperature T_0 is related to the disorder parameters of the system $T_0 = \sigma/k \Sigma$, where σ is the energetic (diagonal) disorder parameter and Σ is the off-diagonal parameter, k is the Boltzmann's constant. For $\sigma = 0.1$ eV and $\Sigma = 3$, $T_0 = 387$ K which is comparable with the experimentally observed compensation temperatures [41]. The microscopic origin of the compensation temperature, where the mobility becomes field-independent, was connected to the competition between energetic disorder, which was assumed to be of Gaussian, and positional, or orientation, disorder [43]. As noted by Schein [2], the occurrence of a temperature T_0 implies an E -dependent hopping factor. Compensation was shown to occur for hopping rates with different intrinsic field dependencies by considering the strong disorder limit. Mobility simulations with Miller-Abrahams hopping rates in which steps to higher energy are activated and rates to lower energy are constant, were most extensively used in MDP simulations. Soos and coworkers [43] used Marcus rates and indicate a low T_0 at low doping in dilute systems. The treatment of Soos and coworkers [43] places position and orientation disorder on equal footing with energetic disorder and brings out their fundamentally different field dependencies. Soos and coworkers [43] conclude that the mobility decreases with E for motion over disordered sites with constant energy. The field shifts the transport to higher-energy sites with faster hopping. Compensation between position or orientation disorder and energetic disorder occurs at some T_0 that depends on the system and rates. They retain the energetic disorder of the GDM but treat position and orientation disorder explicitly and find opposite field dependences that compensate at T_0 .

5 Microscopic models of charge propagation in TOF experiments

The Gaussian disorder model developed by Bässler [25] and verified later by Dunlap *et al.* [35] describes the transport in MDP systems as a biased random walk among dopant molecules with Gaussian - distributed random site energies. In theoretical investigations using the energetic disorder approach it has been shown also how dipolar-disorder can explain not only the high field, but also the low field mobility behaviour [27]. It was shown [35] that both the empirical characterization and the analytical results for one-dimensional transport support the idea that correlated disorder - Charge Dipole Interaction is necessary for obtaining field-dependent mobilities of the Poole-Frenkel type.

A long time debate continues regarding the nature of charge carriers in MDP and other organic solids of a current technological interest [48]. The strong thermal activation of the field dependent mobility μ , seen in the experiments, can arise from a carrier's interaction with phonons (polaron binding), or from peculiar static properties of the material (energetic and spatial disorder). The latter hypothesis was the primary motivation underlying the Gaussian Disorder Model (GDM) of Bässler [25], in which activated mobilities arise from carrier hopping through a Gaussian density of transport states of energetic width $\sigma \sim 0.1\text{eV}$, via Miller-Abrahams hopping [25, 49]. Multiphonon processes typical for polaron transport are, however, absent in this model. Schein and co-workers [2, 16], on the other hand, suggested that carriers are polaronic and crucial to the understanding of the adiabatic to nonadiabatic small polaron crossover. Others combined these viewpoints with carriers assumed to be polarons moving in a disordered medium [26, 43, 50]. However, polaron-based models appear to require unacceptable values of polaron binding energies or transfer integral values in these materials. Parris and coworkers [48] tried to show that this apparent paradox has a natural resolution in light of some recent experimental and theoretical characterization of the correlated, dipolar nature of the disorder through which carriers move in MDP.

5.1 Transport of holes by hopping processes

Pfister [40] claimed that only hole transport can be observed in MDP materials. He also got evidence that holes move by a hopping process and that the transit time, t_{tr} , increases strongly with decreasing dopant concentration ρ and temperature T . He concluded that the strong concentration dependence

on the thermally activated drift mobility of holes, which occurs via hopping, is associated with the dopant molecules and that on a microscopic scale, charge transport in molecularly dispersed systems can be visualized as a transition of an electron from a neutral molecule to the neighboring “molecular cation” (hole transport) or from the “molecular anion” to a neighboring neutral molecule (electron transport). This model suggests that the transport properties vary strongly with the parameters of the dopant molecules, quite differently from transport in the ordered state (molecular crystals), where for a wide range of materials electron and hole mobilities are of the order of $1\text{cm}^2/\text{Vsec}$. Evidently, in the crystalline state where narrow band formation might occur, the influence of the molecular parameters on the transport properties is reduced and one cannot reasonably infer anything about charge transport in disordered solids from the corresponding crystalline data [40].

As a result of the diagonal and off-diagonal disorder, carriers propagating through the bulk of the solid experience a distribution of transit times. Such a distribution can be thought to contribute to dispersion in transient TOF current signals [22]. Yuh and Stolka [22] presented experimental evidence for separating the diagonal and off-diagonal dispersion elements and the field dependent Gaussian dispersive hole transport in MDP represented by N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) molecularly dissolved in polycarbonate (PC). They analyzed the dispersion of charge carrier packets in organic solids also by examining the normalized TOF signals obtained over a wide range of electric fields, sample thicknesses and temperature, and found that carrier dispersion appears to follow the time-dependent Gaussian statistics with a broader Gaussian bandwidth observed at higher electric fields. They explain the Gaussian dispersion by the off-diagonal disorder and the existence of finite field-independent dispersion at very long transit times and the narrowing of the dispersion with increasing temperature by the diagonal disorder, i.e., by a distribution of hopping site energies. All this also implied, however, that a proper theoretical description of the mobility requires a more complete characterization of the disorder. While there is a considerable variety among amorphous molecular solids, their transport properties exhibit certain regularities as seen from the mobility – electric field - temperature dependences [1, 25]. These regularities give hope that a fairly simple uniform model with a modest number of parameters can explain common behavior many of materials [51].

5.2 The disorder formalism and polaron formation

MDPs are understood to be mixtures of electron donor or acceptor molecules in a polymer host in which charge transport involves charge transfer between states associated with adjacent donor or acceptor sites [52]. Many of the latest results on MDP have been interpreted within the disorder formalism given by Bässler and co-workers [1, 25] or by the polaron formation [44, 48, 53, 54]. The disorder theory envisages the charge carrier energy at each hopping site to be randomized with a Gaussian distribution and characterized by an energy width of about 0.1 eV determined by the local environment of the hopping site. The polaron theory assumes that the charge carrier has strong interactions with some of the molecular vibrations of the dopant molecule on which it resides. These interactions self-trap the charge carrier and form the polaron, which can only hop to a new dopant molecule while carrying along its molecular distortion.

While these theories have had success in explaining some aspects of the transport data in MDP, difficulties still exist [2]. For example, the source of the activation energy and, specifically, the magnitude of the contributions due to disorder and polaron formation remain unclear [54]. The activation energy is observed to be independent of ρ in some materials and dependent on ρ in others. The polaron theory can qualitatively account for this observation but the magnitudes of some of the parameters (the transfer integral and the prefactor) needed to explain the data appear unacceptably large [2]. The disorder theory requires the postulation of coincidences or cancellations of opposing effects to account for these observations. The limitation of both theories is also that the electric field dependence $\ln \mu \propto \sqrt{E}$ is experimentally observed in a wider range of fields than predicted by the theory.

To shed further light on the microscopic hopping mechanism in MDP, Schein and Borsenberg [52] have studied the effect of the host polymer on the mobility. Several studies have demonstrated that the polymer host can strongly affect the mobility of MDP and that both the activation energy and prefactor of the mobility can be affected by the polymer host as shown in [52] and references therein. Schein and Borsenberger [52] have chosen to study p-diethylaminobenzaldehyde diphenylhydrazone (DEH) doped into PC and Polystyrene (PS) because it was known that the activation energy is independent of the distance between the hopping sites in DEH-doped PC. This suggests that the interaction of the hopping site with the environment is minimized in DEH-doped PC, thereby allowing the first-order effects of a change in polymer host to be isolated. The data have been systematically

deconvoluted, enabling the effect of the polymer on each of the parameters in the transport equations to be determined independently. They conclude that the field dependence of the mobility is independent of the polymer host hence the first may be independent of the dipole moment of the molecules in the environment of the hopping site. Such a picture is consistent with the small polaron model of hopping. To explain their data within the disorder theory, the width of the hopping should be independent of the hopping distance and the molecular environment.

Considerable debate exists regarding the nature of charge carriers in MDP and other organic solids of current technological interest, as the strong thermal activation of the field dependent mobility μ shown from experiments could arise equally well from a carrier's interaction with phonons by polaron binding, or from static properties of the material due to energetic and spatial disorder [48]. The latter was the primary motivation underlying the Gaussian disorder model (GDM) of Bässler [24] in which activated mobilities arise for carriers hopping through a Gaussian density of transport states with energetic width of $\sigma \sim 0.1\text{eV}$, via Miller-Abrahams hopping. Multiphonon processes typical of polaron transport, are absent in this model. In contrast, Schein and co-workers [2, 16] suggested that carriers were polaronic and that crucial to the understanding of the experiments was an adiabatic to nonadiabatic small polaron crossover.

Hilt and Siebbeles [50] considered both polaron and Miller-Abrahams type jump rates for hopping motion of charge carriers in one-dimensional disordered systems under the influence of an electric DC or AC field by using Monte Carlo computer simulations. They found that charge carrier mobility depends on time because of energy and frequency relaxation of the charge carriers due to asymmetry of the jump rates. They mention that the time and frequency dependence of the AC mobility (obtained from dielectric loss measurements) provide more information on the charge carrier transport mechanism than can be obtained from TOF measurements of mobility only.

Rackovsky and Scher [44] have studied the drift mobility of a molecular polaron in the presence of an applied external electric field and Coulomb traps. Their key result is that the nearly universal experimental behavior of the mobility arises from the competition between the rates of polaron trapping and release from a very low density of Coulomb traps. For a polaron hopping in a molecular system with a Coulomb center and applied field they have calculated the product of the average trapping time τ_{tr} and the average release rate \mathfrak{R} , which is similar to the mobility ratio for semiconductor type drift mobility, $\tau_{tr}\mathfrak{R} = \mu/\mu_0$ [44]. The magnitude of the delay depends on the depth of the carrier in the well. Thus, there is a spectrum of trapping

and release times associated with localized states within a Coulomb center. Rackovsky and Scher [44] suggest that one can associate the average trapping/release time with an energy level range within the well. The choice of this range, or more precisely, the ratio of the transition rates associated with it, is a parameter of their theory. Rackovsky and Scher [44] showed that the field enhances the trapping of the polaron at the Coulomb center, and that this effect can be temperature-independent over a reasonable range. Thus the hitherto inexplicable T_0 term in the phenomenological expression for the mobility (1) can be understood to arise from a similar E -dependence of \mathfrak{R} and the trapping rate $1/\tau_{tr}$. Equations (2) and (3) are consistent with this physical picture: at low T , when escaping is difficult and trapping is easier, the field dependence is governed by release (untrapping) the rate of which should increase with field. At high T , where untrapping is more probable, field-induced trapping leads to the behavior in (2).

On the base of results obtained by the rate spectrum analysis, which enables the disentangling of the separate effects of trapping and release, Rackovsky and Scher [44] conclude that it is plausible to attribute the non-Arrhenius behavior of $\mu(E)$ to the effects of trapping time τ_{tr} . The mobility is not modeled directly by Rackovsky and Scher [44]. It is accounted rather by the expression $\mu/\mu_0 = \tau_{tr}\mathfrak{R} = n/N$, where N and n are the densities of trapped N and mobile n charges, with $n \ll N$ and in order to study the temperature and field dependence of the mobility, the dimensionless product $(\tau_{tr}\mathfrak{R})$ is determined by the trapping (release) of a polaron into (out of) a single Coulomb well.

Parris and coworkers [48] reported on experimental evidence for the necessity of polaronic concepts for the explanation of charge carrier motion in organic materials and assumed carriers to be polarons moving in a disordered medium. They showed that in the presence of correlated disorder, polaronic carriers with binding energies $\sim 50 - 500$ meV and transfer integrals $J \sim 1 - 20$ meV are completely consistent with the magnitudes of observed field and temperature dependences of mobility and that mobilities of MDP are entirely compatible with small polaron motion in a random energy landscape provided it has spatial correlations of the charge-dipole type.

5.3 Monte Carlo simulation techniques

Pautmeier and coworkers [55] used Monte Carlo simulations to study the relaxation of a packet of charge carriers migrating in a Gaussian density of sites of energy width σ . They established that the relaxation time determines

the transition from dispersive to non-dispersive transport seen in a time of flight signal and that dispersive transport occurs if the mean hopping rate of an ensemble of charge carriers generated in a disordered system under non-equilibrium conditions decreases as a function of time. Hopping was assumed to be controlled by the intersite jump rates of the Miller-Abrahams form:

$$\nu_{ij} = \nu_0 \exp\left(-\Gamma_{ij} \frac{\Delta R_{ij}}{a}\right) \begin{pmatrix} \exp\left(-\frac{\varepsilon_j - \varepsilon_i}{kT}\right), & \varepsilon_j > \varepsilon_i \\ 1 & , \varepsilon_j < \varepsilon_i \end{pmatrix} \quad (5)$$

incorporating the electrostatic potential generated between the site energies ε_i and ε_j where $\Delta R_{ij} = R_i - R_j$ and ν_0 are, respectively, the distance between the hopping sites and the characteristic hopping frequency, Γ_{ij} is the wave function overlap parameter and a is the lattice constant [55].

Borsenberger and coworkers [56] recorded the position and energy of the carrier as a function of time, as well as the relevant variances, until the carrier reaches the collecting electrode, averaging over 100-150 carriers, and the only quantity of interest was the average transit time. They also reported that the negative slope in mobility vs. field dependence was found for small fields from simulations for mobility received from average transient times. When the mobility was determined from the intersection of tangents to the photocurrent transients, the range, for which the $\log \mu \propto \sqrt{E}$ relation is observed, was extended to lower fields $4 \cdot 10^5 \leq E \leq 4 \cdot 10^6$ (V/cm). By comparing the experimental results with Monte Carlo simulations, Borsenberger and coworkers [56] concluded that the observed behavior of mobility is a signature of the simultaneous presence of diagonal and off-diagonal disorder and generalized their results providing a framework for determining the magnitude of the relevant diagonal and off-diagonal disorder parameters by analyzing mobility measurements.

Young [51] developed and applied the scaling law and obtained new corrected formulae for the field and temperature dependences implied by simulations for a fairly general class of hopping transport models in the GDM of BäSSLer and co-workers. In his next work on the same theme Young [57] underlines that in spite of the fact that the GDM of BäSSLer and coworkers has had considerable success in accounting for the dependence of the mobility of charge carriers on electric field strength and temperature, the assumption of an accurately Gaussian DOS, used to interpret experimental data in terms of the GDM, is nevertheless questionable. He concludes that within the dipolar-lattice model the GDM is not generally an accurate description of charge transport.

5.4 The macrotrap model of charge transport

Transport is visualized by Kalinovski and coworkers [23] as multitrapping by a quasi-discrete set of spatially extended neutral trapping domains (macrotraps) identified with specific inhomogeneities in the sample, and by hopping between isoenergetic randomly spaced sites disposed between macrotraps. The additional assumption they made was that the DOS profile within macrotraps is an exponential function which, in fact, determines the general shape of the macrotrap potential. A field dependence of the mobility results from a field dependence of the dispersion parameter. No Coulombic traps are required to produce the observed field dependence [23].

The effect of extrinsic traps on the motion of charge carriers in an energetically random hopping system characterized by a Gaussian - shaped density of states function of variance σ has been studied by Wolf and coworkers [7] by Monte Carlo simulations and experiments on tri-p-tolylamine doped PS containing different concentrations of trianisylamine, the known hole trap. They show that the presence of a distribution of traps of the same width but shifted from intrinsic DOS by an energy E_t , does not change the basic phenomenology of hopping transport, as revealed by the dependence of the mobility on temperature and field and their effect can be accounted for via the replacement of σ with an effective width of the DOS whose square increases linearly with E_t and the logarithm of the trap concentration.

Fishchuk and coworkers [29] describe the nondispersive charge-carrier transport in a disordered organic material containing extrinsic traps by an effective medium model. It describes charge transport in the presence of traps more adequately than the conventional Hoesterey-Letson model, which predicts an Arrhenius-type temperature dependence of the charge carrier mobility, where the activation energy is simply the trap depth E_t .

The calculations of Fishchuk and coworkers [29] support the notion that the effect of traps can be quantitatively accounted for by the introduction of an effective disorder parameter σ_{eff} depending on the trap depth and concentration, valid for the whole concentration range. They show also that both relaxation of the ensemble of majority charge carriers within the combined intrinsic and extrinsic density of state distribution and the occurrence of trap-to-trap migration alter the $\mu(T)$ dependence significantly. Notably at lower temperature when the apparent activation energy can become smaller than the trap depth E_t , and $\mu(T)$ is controlled by the width of the distribution of trap levels. If it is narrower than that of the intrinsic DOS, the relaxation of the charge carriers is diminished. As a result, $\mu(T)$ dependence flattens and eventually the mobility in a system containing traps

can exceed that of the undoped system [29].

5.5 Charge localization and transport in disordered materials

According to Blaise [58] the problem of charge localization and transport in disordered dielectric materials has not yet been solved completely. He studied weak localization in the conduction band and its consequences for conduction of electrons injected in insulating materials. He assumed that interband electron transitions are negligible due to the large band gap and impurities do not contribute to conduction as donors or acceptors. In highly disordered insulators such as polymers, it was suggested that multiple trapping is more appropriate for describing the conductivity than hopping because shallow trap states are so rapidly detrapped that the hopping motion through trap states is negligible in comparison. The low drift mobility is thus attributed to the time the carrier spends in traps. The long-term release of the charge from deep traps interpretation is still questionable [58].

Blaise [58], following Anderson theory, accepts that disorder in solid insulators produces localized states causing the charge localization. Blaise based his description of localized states in the conduction band tail on the Mott's formalism to account for conduction properties of these materials. The mobility edge E_c between localized and extended states is located in the conduction band and is a function of the degree of disorder ratio N_c/N , where N and N_c are, respectively, the number of atoms and the number of localized states per unit volume. For $10^{-3} < N_c/N < 10^{-1}$, E_c ranges from $\sim 10^{-2}$ to ~ 1 eV. Blaise deduced conduction from calculations of the Fermi distribution of electrons in the extended and localized states of the conduction band not considering the impurity band. Conduction involves two processes: a hopping one through localized states below E_c with an effective mobility μ_{hop} and a conduction process through extended states above E_c with an effective mobility μ_{ext} . Blaise claimed that when N_c/N increases, μ_{ext} decreases, whereas μ_{hop} increases and the total effective mobility μ exhibits a minimum, the value of which depends on the extension $1/\alpha$ of the wave function characterizing the localized states. He concluded that for a low disorder, conduction is mainly due to extended states, whereas for a high disorder ($> 3 \cdot 10^{-2}$) it is a consequence of hopping through localized states. He concluded also that small variations of disorder around the value $N_c/N = 3 \cdot 10^{-2}$ can change completely the type of conduction from an extended state conduction to a hopping one when N_c/N changes from $N_c/N = 2 \cdot 10^{-2}$ to $N_c/N = 4 \cdot 10^{-2}$. From the data obtained by Blaise

for the temperature dependence of mobility up to 400°K it follows that the extended state conductivity is favored at high temperature.

6 Fitting the experimental TOF transient data to models

Scott and coworkers [59] have suggested that the crucial problem in analyzing the mean mobility in disordered media was the absence of an analytical expression for the time dependence of the current, which can be applied over the entire experimental range.

The task of obtaining a proper parametric quantification of TOF transient currents is not easy since the induced current forms are usually quite complicated and several mechanisms may account for the overall result. Until 1992 there was no analytical expression for the time dependence of the current, which would be generally applicable over the entire range of experimental interest [59]. Scott and coworkers [59], Mirchin and Peled [21, 32, 33, 60, 61] and Hirao [14, 34] proposed similar models to describe the observed transient current shapes. The various methods are described below.

6.1 Analyzing photocurrent transients in terms of an effective normal velocity distribution

Scott and coworkers [59] have proposed a method for analyzing photocurrent transients using two functions, one describing the current, as it would evolve in a semi-infinite sample, and the other accounting for the arrival of carriers at the collecting electrode. They used the Scher-Montroll fractional power law to describe the current, which would flow if the sample were semi-infinite $s_0(t) = A \cdot t^{-(1-\alpha)}$ and reduced it by a factor that accounts for the arrival of carriers at the collecting electrode:

$$s(t) = A \cdot t^{-(1-\alpha)} \left[1 - \int_0^t \frac{1}{\sigma_I t_1^2 \sqrt{2\pi}} \exp \frac{-(1/t_1 - 1/t_0)^2}{2\sigma_I} dt_1 \right], \quad (6)$$

where α is a phenomenological fitting dispersion Scher-Montroll parameter, $0 < \alpha \leq 1$, $\sigma_I = \sigma_v/L$ is the standard deviation of inverse arrival times, σ_v is the width of the velocity distribution, $t_0 = L/\langle v \rangle$ is the mean transit time. They used this functional form for the photocurrent transients to fit

experimental transients for 200 different samples through $215 \leq T \leq 400\text{K}$ and $1 \leq E \leq 120\text{MV/m}$ and obtained $0.65 \leq \alpha \leq 1$ and a relative width ϖ_v of the velocity v distribution $0.3 \leq \varpi_v = \sigma_v / \langle v \rangle \leq 1$ [59]. Their mobility values were considerably lower by a factor of 2 and did not obey the Poole-Frenkel form for the whole electric field range used.

6.2 Photocurrent transients' formalism

Besides the mobility, there are other parameters, such as the charge distribution, the velocity distribution within the packet, and others, which describe the charge transport in organic materials such as MDP, [14, 18, 21, 32–34, 60, 62].

The experimental procedure for measuring the average velocity using the theoretical Photocurrent Transients Equation (PTE) was given by Hirao et al (1995), where additional definitions for the transit time were introduced and their influence on the mobility evaluation discussed. Only the logarithm of the mobility calculated from the transit time as defined from the intersection of the asymptotes to the plateau and the trailing edge had negative field dependence as reported first by Gill ([38] and thoroughly studied by Peled and Schein [41].

A method of obtaining both the velocity v and the diffusion coefficient D from the photocurrent transient has been developed by various researchers [14, 18, 21, 33, 34, 61]. In [34] the following theoretical PTE was proposed:

$$J(t) = \frac{qDn_0}{L\sqrt{4\pi Dt}} \left[\exp \left\{ -\frac{(L-vt)^2}{4Dt} \right\} - \exp \left\{ -\frac{(vt)^2}{4Dt} \right\} \right] - \frac{qn_0v}{2L} \left[\operatorname{erf} \left(\frac{vt}{2\sqrt{Dt}} \right) + \text{Flag} \operatorname{erf} \left(\frac{L-vt}{2\sqrt{Dt}} \right) \right] \quad (7)$$

where n_0 , q and L are the number of holes, the electron charge, and the thickness of the sample, respectively. $\operatorname{erf}(x)$ denotes the error function and $\text{Flag} = \begin{cases} 1, & L \geq vt \\ -1, & L < vt \end{cases}$. The equation is based on the fact that when a carrier packet drifts at a constant velocity it may also spread by diffusion. The mobility μ_a is calculated from the transit time defined as $t_a = L/v$, where v is the velocity defined by fitting the experimental data to the PTE for Gaussian charge profile given by:

$$n = \frac{n_0}{\sqrt{4\pi Dt}} \exp \left\{ -\frac{(x-vt)^2}{4Dt} \right\} \quad (8)$$

or from the time for which the number of arriving carriers at the counter-electrode is maximal, t_r (i.e., the Gaussian packet peak arrival time). Usually the log of the mobility increased linearly with \sqrt{E} [34]. By fitting the photocurrent transients to the PTE, v and D can be obtained simultaneously. The obtained velocity was independent of the film thickness and showed no negative slope field dependence in the low electric field regime [14]. They concluded that the fitting method is suitable to obtain the mobility and tried to explain the behavior of μ_{exp} and the tail broadening parameter W_{exp} using the PTE. By fitting data to this model they showed that the experimental electric field dependence of the diffusion coefficient D has a positive slope.

As mentioned by Hirao *et al.* [14], different kinds of mobilities can be derived from various transit times: (a) the time t_{tr} defined by the intersection of the asymptotes to the plateau and the tail of the transient, (b) the time $t_{1/2}$ a half of the photocurrent decay to its initial value at $t = 0$, and (c) the ensemble average arrival time. However, only the logarithm of mobility derived by the method (a) is proportional to the square root of the electric field while using the log mobilities derived by the methods (b) and (c) were proportional to the square root of the field only in the high electric field region. They also reported experimental results that differ from the above-mentioned simulation [14].

The time t_{tr} corresponds to the time when the current begins to decrease rapidly. If the carrier packet is generated as a thin sheet, the time t_{tr} is approximately the arrival time of the earliest carriers at the counter electrode. The earliest carriers are thought to be transported by a combination of drift and forward diffusion. At the time t_{tr} the sum of the drift length L and the diffusion length L_D is equal to the sample thickness l [21]. Hirao and coworkers [14] tried also to explain the sample thickness dependence of the measured mobility. Since the diffusion length L_D is proportional to \sqrt{t} , its contribution increases with the sample thickness decrease. Finally, μ_{exp} has been shown to have in some cases a thickness dependence [1].

6.3 Modeling of TOF experiments with dispersion and trapping

Our first step towards a better understanding of the charge transport in insulating materials was the proof of the ‘‘Generalized Shockley-Ramo’’ theorem for the displacement current of charge packets [21, 31, 60].

The induced TOF current was investigated analytically for the one-dimensional case of a capacitor type charge transit device structure given in Fig. 3.

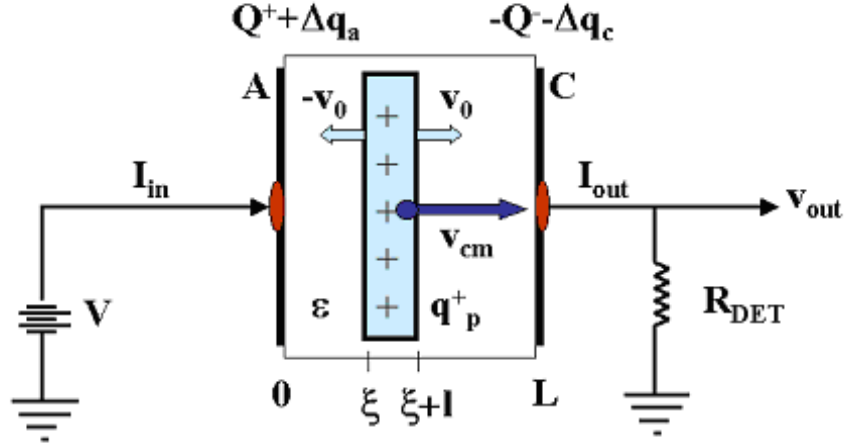


Figure 3: Schematic plot of the a one-dimensional ‘sandwich’ configuration for transit of a charge packet (box shape approximation) in TOF experiments [33]

Using the Generalized Shockley-Ramo theorem developed by Mirchin and Peled [21, 30, 32, 60], we combined the total packet charge, its center of mass velocity and spreading velocities in an analytical result for the induced current on the electrodes with trapping:

$$I(t) = \begin{cases} I_0(t) = \frac{q_{p0}}{L} \cdot \frac{d\xi}{dt} \left[1 + \frac{1}{2} \frac{dl(\xi)}{d\xi} - \frac{l(\xi)}{2L_\tau} \right] e^{-\xi/L_\tau} & , 0 \leq \xi \leq L - l_T \\ I_0(t) \cdot \frac{L - \xi}{l(\xi)} \cdot \frac{1 + \frac{1}{2} \cdot \frac{L - \xi}{l(\xi)} \cdot \frac{dl(\xi)}{d\xi} + \frac{L - \xi - 2l(\xi)}{2L_\tau}}{\left[1 + \frac{1}{2} \frac{dl(\xi)}{d\xi} - \frac{l(\xi)}{2L_\tau} \right]} & , L - l_T \leq \xi \leq L \end{cases} \quad (9)$$

where q_{p0} , l_0 , ξ , L_τ denote, respectively, the initial injected charge, initial charge packet thickness, the back plane moving coordinate $\xi = (v_{cm} - v_0) \cdot t$, and the characteristic trapping length $L_\tau = (v_{cm} - v_0) \cdot \tau$. The characteristic trapping time is τ and L is the sample thickness. v_0 is the spreading velocity of the back and front planes of the charge packet with respect to its center

of mass whose velocity is denoted by v_{cm} . $l(\xi)$ is the instantaneous effective thickness of the spreading packet, and $l_T = l(\xi = (v_{\text{cm}} - v_0) \cdot t_T)$ is the thickness at $t = t_T$, which is the arrival time of the leading edge of the charge packet at the collector electrode. The spatio-temporal development of the charge packet, $l(\xi)$, may accommodate in principle any type of charge packet spreading mechanism. However, the choice of a simple, symmetrical and homogenous spreading form is given by Eq. (10):

$$l(\xi) = 2 \frac{v_0}{v_{\text{cm}} - v_0} \xi + l_0 \quad (10)$$

where l_0 is the initial charge packet width, see Fig. 3.

A normalized form of Eq. (9) has been used for actual data fitting [33]. The normalization was made by designating $I_0 = q_{p0} v_{\text{cm}} / L$ i.e., the simple Shockley-Ramo displacement current of an ideal device without trapping and for a nondispersive infinitely thin packet of charge q_{p0} drifting with the velocity v_{cm} [31].

The DEASP:PC MDP system has been investigated by Mirchin and Peled [30, 32, 33] by fitting the experimental TOF $I(t)$ curves to Eqs. (9) and (10) by using a simple one level trapping model. The electric field and temperature dependencies of all above mentioned parameters μ , v_{cm} , v_0 , τ , L_τ , l_T for this particular MDP system (DEASP 20% and 50%) in PC were found by least error minimization techniques. The T analysis gave a typical value of activation temperature $T_e = T_{cm} \cong 3900\text{K}$, which corresponds to about 0.34eV/atom . We found also a difference in the behavior of v_{cm} and v_0 , i.e., the velocities are similarly activated by temperature but differ with respect to the field dependence behavior. Thus, the transport and spreading mechanisms coincide only with respect to temperature activation and the difference in the electric field dependence must be due to a different mechanism of charge spreading. Indeed, as discussed in [34], based on simulations of the disorder model, diffusion is assisted by electric field for organic insulating materials and its behavior is similar to that of drift mobility obtained in the disorder formalism given by Bässler [25, 63]. However, it was observed [34] that at any specific temperature, $\ln \mu$ is proportional to $\ln D$. Thus one may conclude that $\ln \mu$ is related to $\ln v_{\text{cm}}$ and $\ln D$ is related to $\ln v_0$ which is also in concordance with the disorder formalism in MDP systems.

Relatively few works have studied experimentally trapping in MDP materials [23, 64]. This mechanism, however, is of interest since it has quite a remarkable influence on charge transport in both semiconducting and insulating systems. While mobility applies to the center of mass propagation characteristics, spreading by diffusion combined with trapping can change

remarkably details of the charge carrier interaction processes with the host matrix in transit. Trapping is involved certainly through its dependence on the electric field and temperature and may explain the transiting carriers concentration fluctuations in the sample.

The TOF experiments analyzed according to Eqs.(9) and (10) provide thus a new formalism for the field-temperature dependencies during an effective one charge trapping time τ . Mirchin and Peled [33] observed that $\tau(T)$ and $t_T(T)$ intersect at one point ($T_{\text{intersect}} = 255^\circ\text{K}$) showing that the trapping and transit times at this particular temperature have the same value while at higher temperatures $\tau(T)$ is greater than $t_T(T)$. That is why at high temperatures, trapping in the specific MDP system, DEASP 20% and 50% in PC, can be neglected. This formalism supplied additional information regarding the charge packet width in transit $l_T(\xi)$ and the characteristic trapping length L_τ dependencies on E and T [33]. It was observed, for instance, that the trapping length $L_\tau(E)$ and packet thickness at the collector $l_T(E)$ are almost constant in the intermediate region of electric fields with typical values $L_{\tau_{av}} \approx 10^{-2}\text{cm}$ and $l_{T_{av}} \approx 4 \cdot 10^{-4}\text{cm}$. On the other hand, the trapping length temperature dependence, $L_\tau(1/T)$, exhibits a decreasing exponential shape and the effective thickness of the spreading packet at the collector $l_T(1/T)$ is almost constant within the experimental error with a typical value of $l_{T_{av}} \approx 4 \cdot 10^{-4}\text{cm}$ in the temperature range 227-385°K.

The data obtained by Mirchin and Peled [33] has been used also for evaluating the diffusion parameter D estimated from the total packet width l_T at final transit time t_T , when the charge packet exits at the collector electrode. For this purpose one can use the carrier distribution in a spreading charge packet given by (8) from which the estimation of the characteristic packet width can be taken as the packet width at time t_T , i.e., $l_T^2 \cong 4Dt_T$. Using the experimental E and T dependences of l_T and t_T the following expressions for the diffusion coefficient dependence on field and temperature were suggested [33] :

$$D(E) = \frac{l_T^2}{4t_T} = \frac{l_{0T}^2}{4t_{te}} \exp\left(-2a_{lT}E + a_{te}\sqrt{E}\right) \text{ at } T = 293\text{K} \quad (11)$$

$$D(T) \approx \frac{l_T^2}{4t_T} = \frac{l_{T_0}^2}{4t_{TT}} \exp\left(-\frac{2a_{lTT}}{T} + \frac{T_{TT}}{T}\right) \text{ for } E = 4 \cdot 10^5 \frac{\text{V}}{\text{cm}}, \quad (12)$$

where the following coefficients were obtained by parametric fits of the transit time and final charge packet width for electric field and temperature variations:

$$t_T(E) = t_{te} \cdot \exp(-a_{te} \cdot \sqrt{E}) \text{ with fitting constants } t_{te} = 9.7 \cdot 10^{-3} \text{ sec}$$

and $a_{te} = 8.1 \cdot 10^{-3} \sqrt{\text{cm}/\text{V}}$

$$l_T(E) = l_{0T} \cdot \exp(-a_{lT} \cdot E) \text{ with fitting constants } l_{0T} = 5.2 \cdot 10^{-4} \text{ cm}$$

and $a_{lT} = 2.95 \cdot 10^{-7} \text{ cm}/\text{V}$

$$t_T(T) = t_{TT} \cdot \exp(-T_{tT}/T) \text{ with fitting constants } t_{TT} = 7.97 \cdot 10^{-10} \text{ sec}$$

and $T_{tT} = 4237^{\circ}\text{K}$

$$l_T(E) = l_{0T} \cdot \exp(-a_{lT} \cdot E) \text{ with fitting constants } l_{0T} = 5.2 \cdot 10^{-4} \text{ cm}$$

and $a_{lT} = 2.95 \cdot 10^{-7} \text{ cm}/\text{V}$

The results obtained by Mirchin and Peled [33] when compared with those obtained by Hirao and coworkers [18, 34], show a similar electric field dependence for the diffusion coefficient D . In [34] the log of the diffusion coefficient D increases with \sqrt{E} . However, while the temperature dependence of the diffusion coefficient given by Hirao *et al.* [18] shows also a weak proportionality to $1/T^2$ with small slope on log scale, from (12) and [33] it follows that it is proportional rather to $1/T$.

7 Discussion and conclusions

A great effort has been exerted to develop analytical and numerical methods explaining the experimental conductivity dependence on field and temperature in MDP since the advent of insulator based charge transport devices. Most experimental results on MDP electrical transport considered in the literature use almost solely the concept of electrical mobility borrowed from semiconductor conduction theory. The electric field and temperature dependencies of charge carriers mobility in organic and other non-crystalline materials were always considered as the key to the understanding of the peculiar electronic transport in these materials [1–3, 20, 53, 56].

Unfortunately, neither the field dependence nor the detailed temperature dependence of MDP mobility established from TOF measurements and described analytically by Eq. (1) can be universally explained by the existing models based on charge diffusion, Coulombic spread, trapping or detrapping. In disordered insulators like MDP, there is a priori no justification to assume diffusive spatial spreading mechanisms since no experimental or theoretical indication about thermalized relaxation mechanisms have yet been found. Transport in these materials is now widely assumed to be rather discrete hopping [22, 40, 51] of charge carriers not screened by other charge carriers in the medium. Thus we observe an entirely opposite behavior as compared to semiconductors where carriers are screened, and behave like free in conduction band scattered mainly by phonons and imperfections.

We have reviewed the main trends of investigations, experimental and theoretical, of the electric field, temperature and composition dependences of mobility in such systems [1, 14, 26, 35]. The Gaussian disorder model developed by Bässler [25] and verified later on by Dunlap [35] describes the transport in MDP systems as a biased random walk among dopant molecules with Gaussian distributed random site energies. In these theoretical investigations it has been shown by using the energetic disorder approach that the peculiarities of dipolar disorder can be taken into account to explain not only the high field, but also the low field mobility behavior [27]. In particular [35], the empirical characterization and analytical results for the one-dimensional transport supports the idea that correlated disorder - Charge Dipole Interaction is a necessary ingredient for obtaining field-dependent mobilities of the Poole-Frenkel type. However, the experimental mobility whose logarithm shows proportionality to the square root of the electric field [14] has not yet been explained satisfactorily. Numerical investigations of hopping transport in a disordered matrix were vigorously pursued over the next decade [35]. As a result, it has been shown that the disorder formalism may explain the temperature and electric field dependences of the mobility in MDP providing the disorder is sufficiently large [4].

For the specific DEASP:PC system experimental data, Mirchin and Peled [33] fitted the data obtained from TOF experiments to an electrodynamic formalism [30–32, 60, 61]. The new formalism based on the classical model of charge propagation including deep trapping and spreading allows one to use additional transport and spreading characteristics of the charge packets from the current transients. The interesting results obtained from fitting the experimental data to the new formalism are as follows. The velocity of charge packet spread v_0 has a different field dependence as compared to the center of charge packet mass velocity v_{cm} , with an otherwise similar temperature dependence. The thermal activation energy for both v_{cm} and v_0 parameters was about 0.34 eV. However, for the electric field dependence difference no mechanism has yet been proposed. τ and t_T were found to have a very similar field dependence, i.e., with similar slopes, while the temperature dependence shows a crossover at a well defined temperature above which the deep trapping characteristic time becomes larger than the transit time across the device. Thus, one expects trapping to have a smaller influence on electrical transport at high temperatures. This result is interesting since at high temperatures a diffusing Gaussian space charge distribution is expected to be broadened while the indication is here quite different. The characteristic trapping length L_τ and the final charge packet width l_T are almost constant as functions of electric field being a consequence of the in-

verse dependencies of the velocities and characteristic times on the electric field.

Finally the formalism developed by Mirchin and Peled [21, 30-32, 60, 61], based on Shockley-Ramo's treatment was described as a tool for analyzing dispersive TOF currents in MDP.

The support of this work by the continuing grant obtained from the Israel Ministry of Immigration Absorption under contract No: 280111934 is gratefully acknowledged. The authors are grateful to Alexander Kaplunovsky for his valuable help while preparing this manuscript

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