# Hole Transport in Solid Solutions of a Diamine in Polycarbonate

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Hole transport has been investigated in films of solid solutions of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine in bisphenol A polycarbonate. Charge carrier mobilities in excess of  $10^{-3}$  cm<sup>2</sup>/(V s) have been observed at room temperature at electric fields lower than  $10^4$  V/cm. The values of hole mobility were between  $10^{-10}$  and  $10^{-3}$  cm<sup>2</sup>/(V s) as the molecular concentration was varied from 9 to 100 wt%. At high concentrations of the transport molecule and at fields less than 10<sup>5</sup> V/cm, the mobility is essentially independent of electric field. Field dependence was observed at lower concentrations and higher fields.

#### **Introduction and Background**

Charge transport in amorphous organic materials has been the subject of numerous investigations.<sup>1-19</sup> The early studies were carried out primarily on poly(N-vinylcarbazole) (PVK)<sup>1-5,13</sup> and its complex with 2,4,7-trinitro-9-fluorenone (TNF).<sup>4</sup> The recent studies<sup>7-12,15,17-19</sup> however, described electronic charge transport in several aromatic amines which were molecularly dispersed in inert, inactive polymeric binders. These studies were stimulated by several publications<sup>3,4,7,20</sup> that demonstrated that the polymer backbone in PVK does not participate in transport. The charges are transported by hopping via discrete carbazole groups whether attached to a polymer or not. Seki<sup>20</sup> later associated the hopping site with a discrete uncharged molecule or group and the "hole" with the same molecule or group that is positively charged, a cation radical.

The "molecularly doped" systems became particularly attractive because they enabled studies of the effects of density of localized states which can be varied, at will, by simply changing the molecular concentration of the active component. These systems differ from the classical semiconductors in that the transport is thermally activated, the charge carrier mobilities are generally low  $(10^{-8}-10^{-5} \text{ cm}^2/(\text{V s}))$  and strongly dependent on the electric

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field, and the transit is very dispersive.

There seems to be general agreement that the charge transport in solid solutions of active molecules or active polymers such as PVK is in fact an electric field driven chain of redox processes involving neutral molecules (N) or groups and their charged derivatives: anion radicals  $(N^{-})$  in the case of electron transport and cation radicals  $(N^+)$  in the case of hole transport.<sup>12</sup>



The interpretation of data differs from system to system, but the authors at least agree that the rate of charge transport depends on the type of material, the concentration of active species, temperature, and, most of all, the applied electric field and that the transport is "hopping" in nature and dispersive. Many authors use the term "disordered" organic solids, but we prefer not to use this term since little is really known about the degree of "order" in these materials. There are even indications that some degree of order or alignment of the active species is in fact needed to accomplish charge transfer from one site to another.<sup>16</sup> There still exists considerably controversy as to the reasons for the dispersion of charge carriers in these systems, particularly regarding the actual form of the electric field, temperature, and intersite distance (concentration) dependence.

In crystalline materials, the transient, time-resolved pulse is close to being a rectangle since the carriers travel essentially in a sheet. The only dispersion in the charge packet as it drifts through the film is due to Coulombic repulsion in the sheet of the drifting carriers. In amorphous molecular solids, however, the carriers undergo a broad dispersion as indicated by the shape of transient currents. The dispersion of carriers has been discussed in several publications. $^{6,21-25}$  The dispersive transport observed in most of these materials has been interpreted on the basis of the continuous time random walk theory.<sup>6</sup> It was theorized that small fluctuations in hopping distances and activation energies lead to large fluctuations in hopping times as a result of the exponential dependence of the fluctuations that determine the charge transfer. The theory was broad enough to include large distributions of trap release times in systems with extended-state conduction. The ramifications of these extensions of the individual hopping or trap release times in the transit time range lead to non-Gaussian type dispersion. The shape of the transient current under these conditions is given by the expression

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$$I(t) \propto t^{-(1-\alpha)} \qquad t < t_{\rm T}$$
$$t^{-(1+\alpha)} \qquad t > t_{\rm T} \qquad (1)$$

where  $t_{\rm T} \sim [L/l(E)]^{1/\alpha} \exp(\Delta_0/kT)$ ,  $\alpha$  is a measure of the dispersion with values between 0 and 1, l(E) is the field-dependent mean carrier displacement per hop in the direction of electric field, L is the sample thickness, k is Boltzmann's constant, and  $\Delta_0$  is the activation energy. The transit time in this representation is the point of intersection of two lines on a  $\log i - \log t$  display. According to this model, the charge carrier mobility should vary with the sample thickness, depending on  $\alpha$ . Although the thickness dependence was observed by some authors,<sup>9</sup> measurements by others showed that the charge carrier mobility does not depend on sample thickness.<sup>10</sup> No explanation is available for this discrepancy.

Gill<sup>4</sup> proposed an empirical relationship between mobility and intersite distance  $\rho$  given by

$$\mu \propto \rho^2 \exp(-\gamma_0 \rho) \tag{2}$$

where  $\gamma_0$  is a fitting constant, also known as the localization parameter. This relationship was modified by defining a charge localization radius<sup>4</sup> at the hopping site,  $\rho_0 = 2/\gamma_0$ . The localization radius for a variety of materials is typically 1-2 Å.

This kind of exponential dependence on average intersite distance can be explained in the framework of either (1) nonadiabatic, small polaron hopping<sup>27</sup> or (2) phonon-assisted hopping.<sup>28</sup> In the case of the nonadiabatic, polaron-assisted hopping, the transition rate (proportional to the mobility) is given by

$$W = \frac{J^2}{h} \left( \frac{\pi}{4kT} \Delta \right)^{1/2} \exp\left( \frac{-\Delta}{kT} \right)$$
(3)

where J is the transfer integral which contains the  $\exp(-\rho/\rho_0)$  term. For phonon-assisted hopping,<sup>28</sup> the drift mobility can be ex-

pressed as

$$\mu \propto \rho^2 \exp(-2\rho/\rho_0) \exp(-\Delta/kT)$$
 (4)

where  $\rho_0$ , the charge localization radius, is a measure of the overlap of the wave functions between neighboring dopant molecules. All these expressions assume that the diamine molecules are dispersed uniformly in the binder. All the existing data seem to confirm the above empirical relationship.

The most serious difficulty is encountered in an attempt to describe and explain the field dependence of charge carrier mobility within the framework of existing theories. In conventional semiconductors, the charge transport takes place in extended states. Any electric field dependence of mobility in such systems has been rationalized on the basis of field-assisted lowering of the barrier from Coulombic traps. In such a picture, the carrier drifting through the extended states is trapped at a charged trapping site. The release from the trap is thermally assisted, and the barrier to escape is lowered by the applied electric field. The Poole-Frankel (PF) formalism has been used to describe this phenomenon.<sup>4,29</sup> The lowering of the barrier in this formalism is given by the factor  $\beta_{\rm PF} E^{1/2}$ , where  $\beta_{\rm PF}$  is a constant given by

$$\beta_{\rm PF} = (e^3 / \pi \epsilon \epsilon_0)^{1/2} \tag{5}$$

In this equation, e is the electronic charge and  $\epsilon\epsilon_0$  is the absolute dielectric constant of the medium. If the PF formalism is applicable, a linear relationship should be observed in a log  $\mu$  vs.  $E^{1/2}$  plot. This has indeed been seen for both hole and electron transport in the poly(N-vinylcarbazole)/2,4,7-trinitro-9-fluorenone (PVK/TNF) charge-transfer complex.<sup>4</sup> In spite of a good empirical agreement-at least in the field range studied-the mechanism has been discounted. The model requires the presence of a high density of charged Coulombic centers compensated by oppositely charged centers, essentially in the same density over

the whole range of film compositions. The PF formalism failed in cases of other studied transport systems. Borsenberger et al.<sup>10</sup> found that the mobility follows a linear relationship with the electric field

$$\mu(E) \propto E \tag{6}$$

and that this relationship is independent of concentration. Other investigators<sup>9,19,21,24,25</sup> however proposed more complex, nonlinear relationships between  $\mu$  and  $\dot{E}$ .

According to some recent studies<sup>15,24,25</sup> on simulations of the hopping transport, the mobility in the high-field region should increase exponentially according to the equation

$$\mu(E) = \mu(E=0) \exp(E/E_0)$$
(7)

The equation is based on the assumption that a carrier initially created at random relaxes energetically in the course of its hopping motion to reach an energy level below the average of the available energy states whose energy distribution is assumed to be Gaussian. The average level to which it reaches decreases as the temperature is lowered. Since the carrier motion occurs by thermally activated jumps, the activation energy would be, in the long time limit, temperature dependent, leading to a non-Arrhenius type of temperature dependence given by

$$\mu(T) = \mu(0) \exp(-T_0/T)^2$$
(8)

where  $T_0$  is a characteristic temperature and  $\mu(0)$  is the mobility of a hopping system with no disorder (monoenergetic). A carrier jumping from site i to site j in the direction of the field will gain a field energy  $eE\rho$ . Without a field (E = 0) the carrier would be able to reach a site j with lower energy,  $\epsilon_i < \epsilon_i$ . With the field it will have excess energy to reach, without thermal activation, site j with higher energy than site i as long as  $\epsilon_i < \epsilon_i + eE\rho$ . The net effect of the electric field is, therefore, a reduction of the effective width of the energy distribution by an amount  $BeE\rho$ , where B is a constant that reflects averaging over all hopping directions. Substituting into eq 7 we get

$$\mu(E,T) = \mu_0 \exp[T_0^2/T^2(1 - BeE\rho/\sigma)^2]$$
(9)

For  $BeE\rho/\sigma \ll 1$  and substituting for  $E_0 = (\sigma/2 Be\rho)(T/T_0)^2$ we get

$$\mu = \mu_0 \exp(-T_0/T)^2 \exp(E/E_0)$$
(10)

This equation provides a good fit for data obtained for TPM in polycarbonate.<sup>1</sup>

Another model used to explain the electric field dependence of carrier mobility is based on a kinetic rate theory.<sup>30</sup> The main assumptions of this model are that the electronic carriers are localized discrete chemical species and that the transport is an activated process of charge motion from one site to another with an average energy barrier height  $\Delta$ . The theory says that the electron-exchange frequency between charged and uncharged species in the absence of electric field is

$$k_1 = \nu \exp(-\Delta/kT) \tag{11}$$

where v is the attempt frequency. With an applied electric field, the net jump frequency in the direction of field is

$$f = f_{+} - f_{-} = k_1 [\exp(\rho eE/2kT) - \exp(-\rho eE/2kT)] = 2k_1 \sinh(\rho eE/2kT)$$
(12)

and since the drift mobility,  $\mu$ , is  $\rho f/E$ 

$$\mu = 2(\rho/E)\nu \exp[-\Delta/kT] \sinh(\rho eE/2kT)$$
(13)

This equation suggests that at low fields the mobility is independent of field and at high fields becomes an exponential function of electric field. The high-field dependence of mobility is too shallow on all materials to be represented by this equation.9,19,31

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Figure 1. (a) Schematic of layered structure employed in the time of flight technique. (b) Scheme of the measurement circuitry for time of flight measurements.

The rate theory was later modified<sup>9,12</sup> by incorporating a disorder parameter,  $\alpha$ , so that the final form of the equation is

$$\mu \sim (L/E)^{1-1/\alpha} \sinh (e\rho E/2kT)^{1/\alpha} \exp(-\Delta_0/kT)$$
 (14)

As discussed above, this relationship could only be valid for systems with a disorder parameter  $\alpha$  different from unity, in other words in systems in which mobility depends on the sample thickness. Since the independence on the sample thickness has been demonstrated on at least some materials,<sup>10</sup> and therefore  $\alpha = 1$ , eq 14 would become eq 13 in which case the field dependence of  $\mu$  would be steeper than actually observed.

This brief review clearly shows that there is no universally applicable model for charge transport in amorphous organic solids materials. In this paper we present the hole transport data obtained on films of solid solutions of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine



in bisphenol A polycarbonate and discuss the data in the framework of existing theories. We chose this material because its transport characteristics are such that it allows measurements of transport in broader ranges of electric fields, temperatures, and concentrations than in any other transport material studied thus far. Unlike most known organic transport systems, it forms reasonably stable amorphous glasses in the absence of a polymer binder, thus permitting investigation of transport without the eventual influence of binder media.

### **Experimental Procedures**

The transporting compound, N,N'-diphenyl-N,N'-bis(3methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), was synthesized by a modified Ullmann condensation<sup>32</sup> from N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine and *m*-iodotoluene and purified by extractions into acetone and repeated crystallizations from octane. The drift mobilities were measured by the time of flight technique. The photoconductive device consists of an aluminum substrate on which is vapor deposited a 0.5- $\mu$ m-thick, amorphous selenium (a-Se) layer. A thicker (~20  $\mu$ m) layer of a solid solution of the diamine in polycarbonate resin is solvent coated on top of the a-Se layer. Methylene chloride employed to coat the film is removed by heating the device to 40 °C under vacuum for several hours. A semitransparent gold electrode is then vacuum deposited on the surface of the organic transport layer. The principle behind the time of flight technique is that



Figure 2. Oscilloscope trace of a time of flight signal: x axis, 1 cm = 500  $\mu$ s; y axis, 1 cm = 200 mV (50 wt %, 12- $\mu$ m thickness).



Figure 3. Hole mobilities as a function of electric field for films of different compositions of TPD in polycarbonate.

the holes photogenerated in a-Se by a light flash are injected into and drift through the transport layer as schematically illustrated in Figure 1. The current due to the carrier transit is displayed on an oscilloscope on a double linear axis. A typical transient current pulse is shown in Figure 2. The current is characterized by a sharp pulse at t = 0, a plateau, and a dispersive tail. The sharp current spike at t = 0 is caused by the rapid drift of the photogenerated holes and electrons through the thin amorphous selenium layer. The demarcation point between the plateau and the dispersive tail is defined as the transit time,  $t_T$ , of the initial sheet of carriers. The slow drop-off or the tail following the transit time is caused by the dispersion of the carrier packet as it drifts through the organic film.

There is considerable discussion in the literature regarding the physical processes that give rise to the dispersive tail. Double log plots of transient currents have been suggested to delineate the transit time in situations where the transient current pulses are very dispersive.<sup>10</sup> However, in the diamine system under study, the transit time is clearly discernible in the double linear plots. The charge carrier drift mobility,  $\mu_d$ , is calculated from the ex-



Figure 4. Concentration dependence of the hole mobility.  $\rho$  is the intersite distance.

pression  $\mu_d = L^2/(t_T V)$ , where L is the film thickness and V is the applied voltage.

#### Results

Figure 3 displays representative data for electric field dependence of the charge carrier mobility in films of the diamine dispersed in polycarbonate at several concentrations. The concentration, C, of the diamine is expressed in weight percent. The binder concentration is then 100 - C. Amorphous films of TPD in polycarbonate have practically unlimited stability under ambient conditions. No crystallization has been detected by the differential scanning calorimetry method. Even films with 80 wt % TPD and solid amorphous glass films of 100 wt% TPD have sufficient stability to perform measurements before any crystallization is detected. Figure 3 also shows data for a solid amorphous glass film of 100 wt % TPD. Measurements have also been made on films containing less than 25 wt % TPD. Clear transient signals have been observed with films containing as low as 9 wt % concentration of the molecules. Mobilities in these films were near  $10^{-10} \text{ cm}^2/(\text{V s}).$ 

With this system, it is possible to detect clear transit times down to very low fields on transient current curves displayed on a double linear axis. The low-field limit to the data points is set by the signal-to-noise ratio and not by any trapping in the TL. The shape of the time of flight transient current remains stable and invariant when the device is exposed to multiple light flashes with the electric field on. This indicated that the TPD/polycarbonate films are essentially "trap free". The data from Figure 3 and the data for films containing lower concentration of the diamine are replotted in Figure 4 as a function of the average separation distance between molecules. The low-field mobility values from the fieldindependent portion of the plots in Figure 3 are used in Figure 4. An exponential relationship between  $\mu/\rho^2$  and  $\rho$  is observed. The localization radius  $\rho_0$  calculated from eq 2 is 1.4 Å. It should be noted however that the value of  $\mu/\rho^2$  obtained for 100 wt % diamine is significantly above the straight line extrapolated from values for other intersite distances.

The average distance,  $\rho$ , between molecules is calculated from the formula  $\rho = (M/(Ad))^{1/3}$ , where M is molecular weight (516), d is the density (1.2), and A is Avogadro's number (6 × 10<sup>23</sup>). The average distance,  $\rho$ , between molecules in a glass sample





Figure 5. Field dependence of hole mobility in amorphous solid glass of TPD at various temperatures.



Figure 6. Arrhenius plot of hole mobility in glass of 100 wt % TPD at different electric fields.

containing 100 wt % diamine is therefore 9 Å. The average separation distance of 20 Å in Figure 4 corresponds to 9 wt % of the diamine.

Figure 5 shows the hole mobility as a function of electric field at different temperatures for a sample containing 100 wt % diamine. The field dependence becomes steeper as the temperature is lowered. The upper temperature limit of data collection is given by the crystallization of the a-Se used as the carrier generator. The lower temperature limit is again set by the signal-to-noise considerations. To obtain the activation energies  $\Delta$ , we replotted the data from Figure 5 as functions of temperature for different electric fields (Figure 6). The curves show an inflex at the high-temperature end of the measurement which seems to indicate a change of activation energies. The activation energy of hole transport becomes lower at higher temperatures. The data in Figure 6 are replotted in Figure 7 on a logarithmic scale against  $T^{-2}$ . Solid lines are drawn through the data points, and their extrapolation to the high-temperature end is indicated by the dashed lines. The lines for different fields appear to intersect at T = 381 K. Figure 8 shows the hole mobility vs. electric field in a film of the solid solution of the diamine in polycarbonate containing 80 wt % of the diamine, for different temperaures. The range of data at low temperatures is limited by the signal-to-noise



**Figure 7.** Log  $\mu$  vs.  $(1/T)^2$  dependence for glass of 100 wt % TPD at different electric fields.



Figure 8. Field dependence of hole mobility in 80/20 TPD/polycarbonate films.

ratio. The field dependence again becomes steeper as the temperature is lowered. Figure 9 shows a family of curves, parametric in temperature, depicting the field dependence of mobility in a log  $\mu$  vs. *E* formalism for a film of 60/40 TPD/polycarbonate. Within experimental errors, a linear relationship is observed. An



Figure 10. Arrhenius plot of  $\mu$  for 60/40 TPD/polycarbonate films at various fields.

Arrhenius plot of the temperature dependence of the mobility for the same film is plotted in Figure 10. The plot shows that the activation energy changes at about room temperature, at all electric fields. The corresponding log mobility vs.  $(1/T)^2$  plot is



Figure 11. Log  $\mu$  vs.  $(1/T)^2$  plot for 60/40 TPD/polycarbonate films at different electric fields.



Figure 12. Concentration dependence of activation energy,  $\Delta$ , at two different electric fields.

shown in Figure 11. Again, within experimental errors, the relationship appears to be linear. However, these extrapolated lines intersect at T = 408 K which is different from that observed for films of 100 wt % TPD (Figure 7). For 50 wt % TPD the lines intersect at T = 478 K. Figure 12 shows the low- and high-field mobility activation energies as a function of the intermolecular distance in the films. The activation energy increases with the intersite distance with most of the increase occurring between the films with 100 and 80 wt % TPD. The activation energy decreases with increasing electric field above  $\sim 5 \times 10^4$  V/cm. Below that field, the activation energy is independent of field. Figure 13 shows the hole mobility vs. film thickness in films containing 50 wt % TPD. The mobility is independent of thickness to at least 90  $\mu$ m.

#### Discussion

Charge transport in solid solutions of transporting molecules in polymeric binders is an electronic process<sup>12</sup> since the electron exchange proceeds among stationary molecules and no displacement of matter is involved. This can be argued, however, since from the chemical kinetics point of view, the charged molecule (cation radical, a "hole") and the interacting neighboring molecule



Figure 13. Film thickness of hole mobility in 50/50 TPD/polycarbonate films.

must come to an effective "collision" distance before the reaction (electron exchange) can occur. It is therefore conceivable that the charged molecule (anion) migrates in the direction of electric field over a small distance of several angstroms, as the medium viscosity and void concentration permit, to reach the effective collision distance to the neighboring molecule. The experimental techniques applied in this study do not differentiate between the purely electronic transport and transport caused by ionic migration. Most of the transport, however, is electronic, and the possible contribution of the ionic displacement can be neglected. If the distance is too large, the electron transfer becomes improbable and eventually no charge transport is seen in the absence of the diamine molecules.

The charged molecule and its uncharged counterpart must be favorably oriented with respect to each other. If the mutual orientation is not favorable for electron transfer, the site may become a "conformation trap".<sup>5</sup>

For hole transport, it is essential that the molecules—or groups if attached to a polymer chain—are electron donors in nature, have low ionization potentials so that they easily form the cation radicals by transfer of an electron to photoexcited selenium, and that the redox process oxidation/reduction/oxidation is completely reversible. If some degree of irreversibility is encountered, for example, if the cation radical undergoes a chemical restructuring or loses a group etc., that positive charge would not be filled with an electron from a neighboring neutral molecule and could under certain circumstances act as a trap. Cyclic voltammetric study of TPD showed that the one-electron redox process is completely reversible; the oxidation is not followed by any chemical reaction.<sup>33</sup>

Charge carrier mobilities in amorphous organic systems have been found to be generally dispersive, low, thermally activated, and electric field dependent. The data obtained on the diamine system are generally no exception, although there are some differences. The similarities and differences will be discussed next.

The shapes of the transit pulses in a qualitative sense were not always reproducible between samples although the transit time was clearly discernible and reproducible within the limits of experimental error. No attempt has also been made to determine the slight variability in the pulse shape between samples. No attempt has been made to study the temperature or field dependence of the shape of the transit pulses.

From the chemical kinetics point of view, it is expected that the charge carrier mobility will depend on the concentration of the active molecules or, in other words, on the average distance between the active sites (molecules). The hole mobility of TPD is indeed strongly concentration dependent. Figure 4 suggests that, for concentrations lower than 80 wt % or for an average intermolecular distance larger than 9.6 Å, the empirical relation (given by eq 2) seen in other materials is valid. Approximately doubling the average intersite distance from 9 to ~20 Å causes ~10<sup>7</sup>

<sup>(33)</sup> F. Saeva and J. Facci, private communication.

reduction in charge carrier mobility. The deviation from this experimental relationship for 100 wt % TPD (intersite distance ~9 Å) will be discussed later. In eq 2,  $\rho$  is the average intermolecular distance between the molecules and  $\rho_0$  is defined as a localization radius. A value of  $\rho_0 = 1.4$  Å was calculated from Figure 4. This value is similar to those obtained for triphenylamine in polycarbonate<sup>10</sup> (1.8 Å), N-isopropylcarbazole in polycarbonate<sup>7</sup> (1.5 Å), 2,4,7-trinitrofluorenone in a polyester<sup>3</sup> (1.8 Å), and bis[(diethylamino)-2-methylphenyl]phenylmethane in polycarbonate<sup>19</sup> (1.5 Å). As mentioned in the Introduction, filmthickness-dependent mobility was predicted and subsequently experimentally verified in some systems<sup>34,36</sup> but not observed by others.<sup>10</sup> Within experimental errors as shown in Figure 13, the mobility in the diamine system is independent of film thickness, over a wide range of thicknesses. The experimental data presented in this work, however, were obtained on a double linear plot since a transit time is clearly discernible. In the published literature where the thickness dependence was observed, the transit times were generally difficult to measure. In those cases the transit times were determined from the double log plot of current vs. time.

Around ambient temperature, the hole mobility in TPD is essentially independent of electric field over a wide range of concentrations. In that sense, the diamine system seems to be different from other systems reported to date. It should be pointed out, however, that in most of the organic materials in which mobility data have been reported the mobility is field dependent in the narrow range of fields in which the data have been recorded. It is, therefore, possible that the mobility in these materials is independent of electric field at fields too low to permit measurements due to signal-to-noise limitations. In that respect, all materials may exhibit field-independent mobility in very low regions of the electric field. The difference may lie in the value of the electric field at which the observable field dependence begins.

The dependence of log  $\mu$  on  $E^{1/2}$  is not linear for TPD which further indicates that the Poole-Frankel formalism is not applicable for this system. The electric field dependence cannot be described by eq 13 either since the field dependence is too shallow. The independence of  $\mu$  on thickness also invalidates the relationship given by eq 14 for this material. At least at high fields this system seems to be best described by the relationship<sup>15</sup>

## $\mu = \mu_0 \exp(E/E_0)$

As indicated in Figure 5, for T < 300 K the temperature dependence of the hole mobility can be reasonably approximated by an Arrhenius representation with a field-dependent activation energy. This form of temperature dependence has been observed with all disordered molecular solids. All the models discussed above predict some activation energy which could be generalized to include field dependence. In the Poole-Frankel picture, the trap depth is lowered by the applied field, and this accounts for the field-dependent activation energy. However, we have discounted this model on the basis of the observed field dependence of the mobility. The computer simulations of a Gaussian distribution of hopping sites have shown the temperature dependence to be  $\mu = \mu_0 \exp(-T_0/T)^2$ , where  $T_0$  is proportional to the Gaussian width. Equation 10 is valid in the presence of the electric field. If this is true, the display of mobility data on log  $\mu - T^{-2}$  plots should yield a family of straight lines converging to a common ordinate intercept at  $\mu = \mu_0$ . Figure 7 for amorphous diamine and Figure 11 for a film of the diamine in the binder might seem to suggest that the mobilities on log  $\mu - T^{-2}$  representation are a family of straight lines that intersect at one point. However, the point of intersection does not lie on the ordinate. Moreover, the temperature at the point of intersection varies with the film concentration. The computer simulation model may have to be modified and other shapes and widths of the energy states con-

#### sidered to explain these features.

The temperature data, therefore, cannot be adequately explained on the basis of any of the models published and discussed thus far.

The temperature dependence has several interesting features. One feature can be seen in the Arrhenius representation of Figures 6 and 10 where a change in the activation energy is observed for T > 300 K. Such changes in activation energy have also been observed in several amorphous molecular solids and have been attributed to the glass transition temperature of the organic solid solution.<sup>14</sup> In the computer simulation model discussed earlier, it is assumed that the width of the energy distribution is changed by the onset of the thermally induced dynamic effects near  $T_g$ . On the other hand, if transport is due to trap-controlled hopping, dynamic effects near  $T_g$  may increase the number of structurally induced shallow traps and thereby adversely affect the mobility. These are reversible effects on long time scale.

The second interesting feature that has not been reported for any other amorphous organic transporting material is seen in Figure 12. A significant change in the overall activation energy is observed between the amorphous diamine film and a film containing the binder. A slight change of intermolecular distance from 9 to 9.6 Å between the amorphous diamine film and a film containing 80 wt % diamine produces approximately a twofold increase in the activation energy. Further dilution of the solid, although causing significant change in the intermolecular distance, produces a very gradual change in the activation energy. A corresponding steep increase in mobility between the amorphous film and a film containing 80 wt % diamine is also observed in Figure 4. In the framework of the nonadiabatic, small-polaron hopping model, the lower activation energy for the amorphous diamine system may be connected with the intermolecular overlap term  $\exp(-\rho/\rho_0)$ . In an amorphous solid, the overlap may be significant and may be the dominant mechanism. However, in films diluted with even a small concentration of polycarbonate, the rotational overlap might be equally significant and may contribute to an activation energy.

A third interesting feature is that, in the field-independent region of the mobility, the activation energy is also independent of the applied field. This has not been observed with any other organic amorphous system, but it is to be expected for systems in which the mobility is field independent.

Finally, a deviation from the exponential dependence of  $\mu$  on the intersite distance (eq 2) is observed at high concentrations of TPD (Figure 4). The deviation becomes significant when the average intermolecular distance approaches the maximum molecular dimensions. At these high concentrations the charge transport may be enhanced by percolation.<sup>37</sup> A similar phenomenon has been observed in TNF systems.<sup>3</sup> A significant decrease in the apparent activation energy at these concentrations may be connected with the change in the transport mechanism.

## Conclusions

The charge transport in solid solutions of diamine in polycarbonate occurs through a chain of redox processes involving an overlap between the neutral molecule and its cation radical in their ground state. The overlap is easily varied by changing the average intermolecular distance by varying the concentration of the active molecules. Except at very short intermolecular distances, the charge carrier mobility drops exponentially with the intermolecular distance. Since the overlap between the neutral molecule and its cation radical changes with the orientation of the molecules, the mobility is found to be temperature dependent. Mobilities in excess of  $10^{-3}$  cm<sup>2</sup>/(V s) have been observed at room temperature and at electric fields below 10<sup>4</sup> V/cm. These values far exceed those reported to date for any amorphous organic system. In common with other amorphous organic solid solutions studied to date, the mobility is electric field dependent when measured in a wide range of electric fields and temperature. However, around room temperature, the hole mobility in the diamine system is essentially

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independent of the electric field for a wide range of concentrations. In this respect, TPD differs from all systems studied thus far. The field dependence at high fields can be best described by the exponential relationship proposed by the computer simulation of hopping transport.<sup>24</sup> Some disagreement however still exists with the temperature dependence predicted by the model. The field

and temperature dependence of the mobility in the wide ranges in which the measurements were performed cannot all be explained in the framework of existing theories.

Registry No. TPD, 65181-78-4; bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A) · (carbonic acid) (copolymer), 25037-45-0.

# Trap-Controlled Hopping Transport

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Transition from hopping to trap-controlled hopping transport has been observed in poly(N-vinylcarbazole) (PVK) doped with another transporting material, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD). At very low concentrations of the additive, the transport is dominated by the slow release of charges from the additive sites acting as traps for transport via carbazole groups of the polymer. As the concentration of the additive is increased, the transport is dominated by hopping via the additive sites with the polymer acting as an inert binder. The large trapping effect of small concentrations of TPD is explained on the basis of the difference in ionization potentials of the two materials.

#### Introduction

Charge transport in crystalline solids takes place in extended states, and the microscopic charge carrier mobility  $\mu_0$  is determined by the nature of the band and the scattering the carrier experiences as a result of crystal lattice vibrations. In the presence of shallow traps, the free carrier motion is interrupted by the interaction with the traps. The number of trapping events during the course of the drift depends on the concentration of traps. As a result, at any given time, a fraction  $[n_{t0}/(n_{t0} + n_0)]$  of carriers in transit reside in shallow traps, and the remaining carriers  $(n_0/(n_{t0} + n_0))$ are "free". The transit time in the presence of shallow traps is equal to the sum of microscopic transit time "while free" and the product of the number of trapping events a carrier experiences during transit and the trap release time. The drift mobility is then<sup>1</sup>

$$\mu = \mu_0 [n_0 / (n_{\rm t0} + n_0)]$$

where  $\mu_0$  is the microscopic mobility,  $n_0$  is the number of free carriers, and  $n_{t0}$  is the number of carriers residing in the shallow traps. Trap-controlled drift mobilities have been reported in a number of inorganic and organic crystals.<sup>2,3</sup>

On the other hand, charge transport in amorphous organic solids is a hopping process.<sup>4-6</sup> It is dominated by conditions for charge exchange between neighboring hopping sites, which are discrete molecules or groups if the material is a polymer. It is tacitly assumed that the distribution of energy of hopping sites in "trap-free" hopping systems is narrow, and therefore approximately the same amount of thermal activation is needed to free charges from all the hopping sites. It is estimated<sup>7</sup> that the energy distribution width is only about 0.1 eV.

Trapping then should mean the presence of hopping sites that differ from the majority of sites in that they require substantially larger energy input to release the charge carriers back to the majority type of hopping sites.

On the basis of these considerations it was proposed that hole transport via one molecule would be affected by trapping on

another molecule provided the latter has lower ionization potential.<sup>8</sup> This was indeed demonstrated by results obtained with N-isopropylcarbazole (NIPC) and triphenylamine (TPA). Both materials display comparable charge transport characteristics<sup>8</sup> when dispersed individually in inert polymeric binders. Both have field-dependent carrier mobilities which are thermally activated. Since the gas-phase ionization potential of TPA is 0.48 eV lower than that of NIPC, TPA when present in small concentrations can become trapping molecule for transport via NIPC.

In this paper we describe hole transport in two materials with markedly different transport characteristics, poly(N-vinylcarbazole) (PVK) and N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD).



Charge transport in PVK has been studied extensively.<sup>9-11</sup> The carrier mobility is strongly field dependent in the whole range of measured fields and typically low, from  $\sim 10^{-8}$  to  $\sim 10^{-5}$  cm<sup>2</sup>/(V s), depending on the temperature and electric field. The activation energy of hole transport<sup>11</sup> at  $E = 5 \times 10^5$  V/cm is ~0.4 eV and also field dependent.

The hole mobilities in TPD are independent of electric field up to  $\sim 10^5$  V/cm, particularly at high concentrations of TPD in the polymer matrix and in amorphous glass of TPD.<sup>12</sup> Values of  $\mu$  exceeding  $10^{-3}$  cm<sup>2</sup>/(V s) have been measured even at electric fields well below  $10^4 \text{ V/cm}$ . The apparent activation energy of hole transport in the amorphous glass of TPD below  $T_g$  (63 °C) is only 0.12 eV.

#### **Experimental Section**

The synthesis and purification of N,N'-diphenyl-N,N'-bis(3methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) has been described in the previous publication.12 PVK was purified by fivefold

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