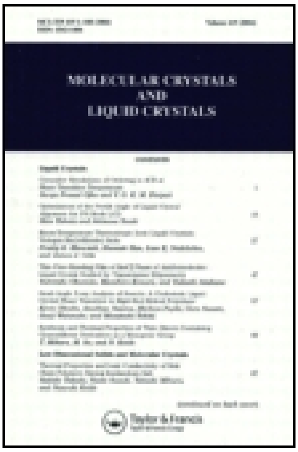

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Charge Transport in Disordered Molecular Solids

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CHARGE TRANSPORT IN DISORDERED MOLECULAR SOLIDS

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Abstract Hole transport has been investigated in a series of vapor deposited donor compounds. The results are described by the disorder formalism, due to Bässler and coworkers. According to the model, transport occurs by hopping through a manifold of states subject to energetic and positional disorder. Key parameters of the model are σ, the width of the density-of-hopping sites, and Σ, a parameter that describes the degree of positional disorder. The results show that σ increases with increasing dipole moment of the donor molecules. The effect is attributed to random electric fields associated with dipole moments of the donor molecules. The degree of positional disorder is shown to be considerably less than that for doped polymers containing the same donor compound. The implication of these results to transport phenomena in doped polymers is briefly discussed.

Molecularly doped polymers contain a strong electron donor or acceptor molecule in a host polymer. Hole or electron transport occurs by the transfer of charge between adjacent donor or acceptor molecules, respectively. Due to the widespread use of doped polymers as xerographic photoreceptors, there have been many studies of transport phenomena in these materials during the past two decades.[1,2] Mobilities of doped polymers are strongly temperature and field dependent, as well as dependent upon the donor or acceptor molecule and the polymer host.

Many recent observations have been shown to agree with predictions of the disorder formalism, due to Bässler and coworkers.[3-6] According to the formalism, transport occurs by hopping through a manifold of states subject to concurrent energetic and positional disorder. At high fields, the model predicts the mobility is

$$\mu(\hat{\sigma}, \Sigma, E) = \mu_0 \exp\left[-\left(\frac{2\hat{\sigma}}{3}\right)^2\right] \exp\left[C\left(\hat{\sigma}^2 - \Sigma^2\right)E^{1/2}\right], \tag{1}$$

where σ is the width of the density-of-states, DOS, $\hat{\sigma} = \sigma/kT$, Σ a parameter that characterizes the degree of positional disorder, E the electric field, μ_0 a prefactor mobility, and C an empirical constant given as 2.9×10^{-4} $(\mathrm{cm/V})^{1/2}$. The key predictions of Eq. (1) are the field dependencies of the high field mobility and the temperature dependence of the zero-field mobility. A further prediction is that slopes of the field dependencies at high fields ($\beta = \partial \ell n(\mu/\mu_0)/\partial E^{1/2}$) should be linearly dependent upon $\hat{\sigma}^2$ with a slope given as C. As C contains no adjustable parameters other than intersite distance, such a comparison provides a critical test of the model. Predictions of the model agree with results observed in a wide range of molecularly doped[7,8] as well as main chain polymers such as the polysilanes[9] and poly(2-phenyl-1,4-phenylene-vinylene).[10]

The fundamental parameters of the disorder model are σ and Σ. The width of the DOS is determined by interactions of the localized carrier with the surrounding molecules. The largest of these is assumed to be charge-dipole interactions. In highly polar materials, these may be expected to dominate. In agreement with this hypothesis, Suginuichi[11] has demonstrated that mobilities of a wide range of donor molecules doped into a polymer host are strongly dependent on the dipole moment of the donor molecule. Further, dipolar disorder[12,13] and polymer polarity arguments[14,15] have been recently invoked to explain the role of the polymer host on hole mobilities of a series of doped polymers.

To further elucidate the role of dipolar disorder, it is of interest to study transport phenomena in materials where the complications of a polymer host can be neglected. Materials that are appropriate for such a study are donor or acceptor compounds that can be prepared as amorphous films by vapor deposition techniques. A series of donor compounds which can be prepared in such a manner include 1-phenyl-3-p-diethylamino-styryl-5-p-diethylphenylpyrazoline (DEASP), p-diethylamino-benzaldehyde-diphenyl-hydrazone (DEH), bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane (MPMP), and 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC). The dipole moments of these materials are 4.34 Debye (DEASP),[11] 3.16 Debye (DEH),[16] 1.79 Debye (MPMP),[16] and 1.0 Debye (TAPC).[16]

Figure 1 shows the field dependence of the mobility for DEASP measured at 0.95 T_g and 1.05 T_g. For DEASP, T_g is 320 K. As observed in a wide range of doped polymers, the field dependence of the mobility can be described as $\exp(\beta E^{1/2})$ where β is a constant that decreases with increasing temperature. The same field dependence is observed both above and below T_g. Figure 2 shows the temperature dependence of the zero-field mobility. The zero-field values were obtained by extrapolating the high field values to $E = 0$. Describing the results as $\mu = \mu_0 \exp{-(T_0/T)^2}$ gives $T_0 = 819$ K. In the disorder formalism, σ is related to T_0 as $\sigma = 3kT_0/2$, hence the experimental value of T_0 corresponds to $\sigma = 0.110$ eV. A further prediction of the model is that β ($\beta = \partial \ell n(\mu/\mu_0)/\partial E^{1/2}$) versus $\hat{\sigma}^2$ should be linear with a slope given as C (2.9×10^{-4} $(\mathrm{cm/V})^{1/2}$). Figure 3 shows the results. The temperature range for which these measurements can be performed is approximately 318 to 230 K. The high temperature limit is determined by the glass transition temperature. For temperatures below 230 K, transit times cannot be derived from double linear current versus time plots. Over the accessible

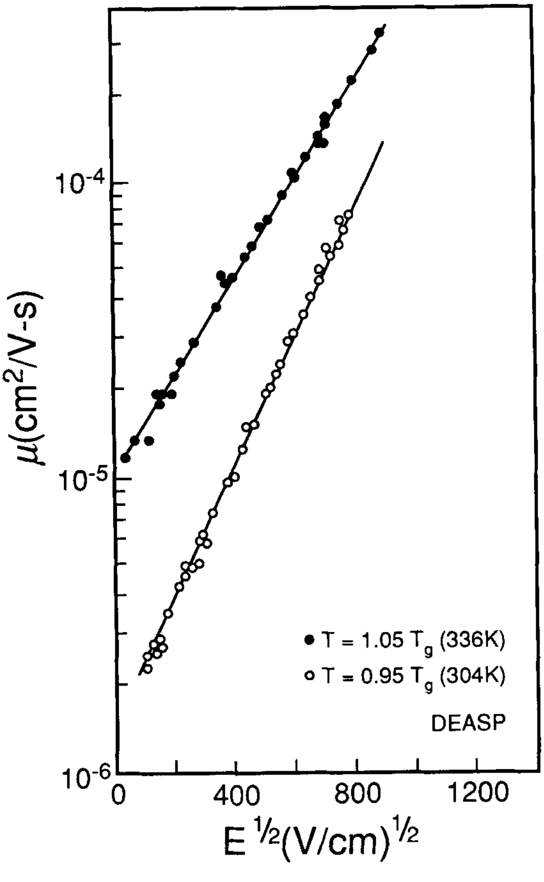

FIGURE 1 The field dependence of the hole mobility in DEASP.

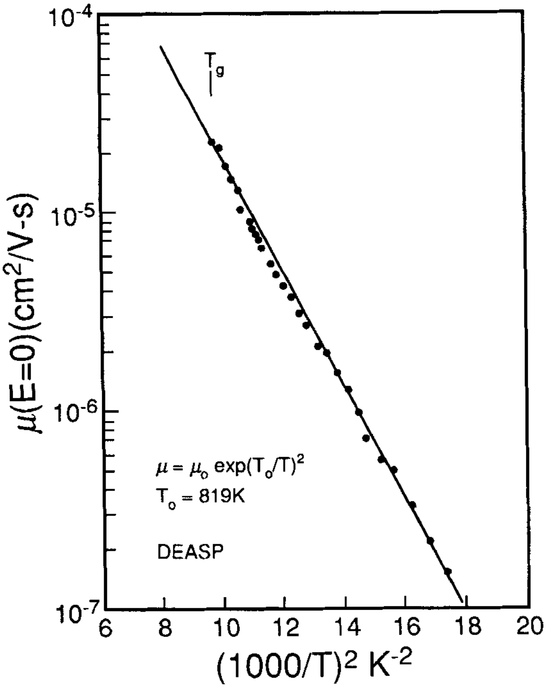

FIGURE 2 The logarithm of the zero-field mobility versus T^{-2} for DEASP.

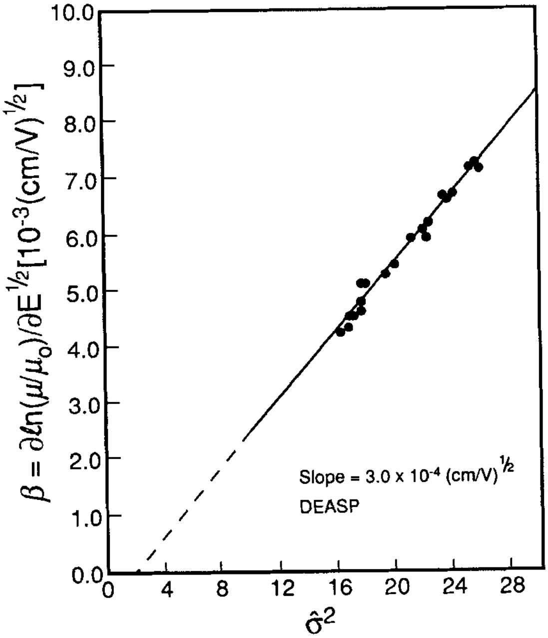

FIGURE 3 β versus $\hat{\sigma}^2$ for DEASP. Here $\beta = \partial \ell n(\mu/\mu_0)/\partial E^{1/2}$ and $\hat{\sigma} = \sigma/kT$.

range of temperatures, however, β is linear in $\hat{\sigma}^2$. The experimental value of the slope is 3.0×10^{-4} $(cm/V)^{1/2}$, in agreement with the value derived by simulations. From the $\beta = 0$ intercept, Σ is determined as 1.4 from the condition $\hat{\sigma}^2 = \Sigma^2$. By similar techniques, values of σ and Σ have been determined for DEH, MEMP, and TAPC. The results are summarized in Table 1.

TABLE 1 Hole transport parameters.

Compound	Dipole moment (Debye)	σ (eV)	Σ
DEASP	4.34	0.110	1.4
DEH	3.14	0.104	2.0
MPMP	1.79	0.098	2.0
TAPC	1.00	0.068	1.0

The results illustrated in Figures 1-3 show that the field dependence of the mobility, the temperature dependence of the zero-field mobility, and the temperature dependence of the field dependencies of the mobility agree with predictions of the disorder model. The model thus provides a self-consistent interpretation of the principal experimental observations. The data suggest a correlation between the width of the DOS and the dipole moment of the donor compound. The results are illustrated in Figure 4. While the effect of dipolar disorder is believed to be of intermolecular origin, it is noted that the width of the DOS of doped polymers is considerably larger than the corresponding donor compound in the absence of a polymer. Further, the width of the DOS for doped polymers may be dependent on the concentration of the donor compound. These observations suggest that other factors may contribute to the width of the DOS in doped polymers. Of these, fluctuations of intersite distances and variations of molecular geometry are considered to be the most likely. Finally, it is noted that the positional disorder parameter, Σ, is significantly less than for doped polymers. For doped polymers, values of 2 to 4 are typically observed. The differences are suggested as due to packing constraints induced by the polymer host.

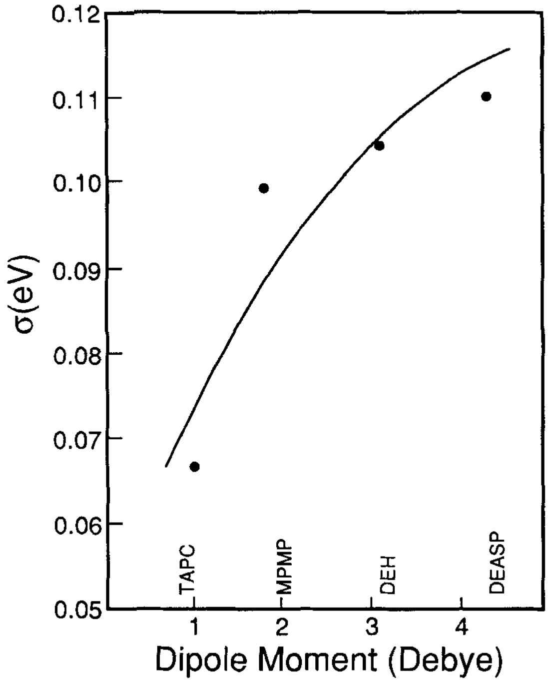

FIGURE 4 σ versus dipole moment for TAPC, MPMP, DEH, and DEASP.

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