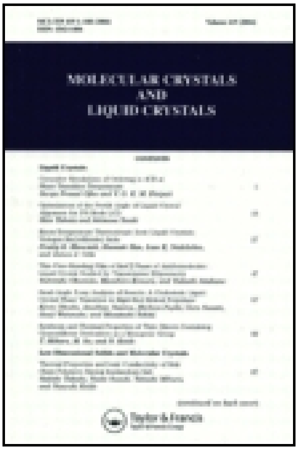

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HOLE DRIFT MOBILITIES IN THE GLASSY STATE OF ARYLALDEHYDE AND ARYLKETONE HYDRAZONES

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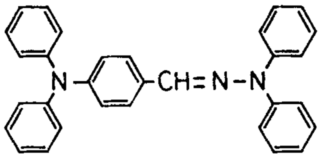
Abstract Hole transport in the glassy state of arylaldehyde and arylketone hydrazones, 4-diphenylaminobenzaldehyde diphenylhydrazone (DPH) and 4-diphenylaminoacetophenone diphenylhydrazone (M-DPH), has been studied. The values of the hole drift mobility in the glassy state of DPH and M-DPH are over one order of magnitude greater than those of 50 wt% molecularly dispersed systems in polycarbonate. The hole drift mobility of DPH is ca. twice as high as that of M-DPH. Temperature and electric-field dependencies of the hole drift mobilities in the glassy state are discussed.

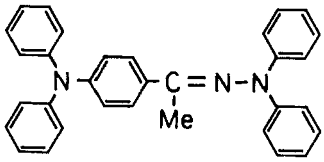
INTRODUCTION

Charge transport properties of molecularly doped polymers have been a subject of recent extensive studies for both academic interest and practical applications as photoreceptor materials in electrophotography.[1-4] However, few studies have been made of charge transport in the amorphous glassy state of low-molecular-weight organic materials,[1] because low-molecular-weight organic compounds generally tend to form crystals. It is expected that amorphous molecular materials that form stable glasses will form films without polymer binders and provide information on their intrinsic properties in the amorphous glassy state.

We have found that a series of arylaldehyde and arylketone hydrazones constitute a new class of amorphous molecular materials that form stable glassy states above room temperature on cooling from the melt.[5] We report here hole transport properties of arylaldehyde and arylketone hydrazones in their amorphous glassy states. The compounds studied in the present study are 4-diphenyl aminobenzaldehyde diphenylhydrazone (DPH) and 4-diphenylamino-acetophenone diphenylhydrazone (M-DPH).



DPH



M-DPH

EXPERIMENTAL

Materials

The arylaldehyde and arylketone hydrazones, DPH and M-DPH, were prepared by the reaction of diphenylhydrazine with 4-diphenylamino-benzaldehyde or 4-diphenylaminoacetophenone in ethanol, which were derived from Vilsmeier reaction or Friedel-Crafts acylation of triphenylamine, and purified by silica-gel column chromatography, followed by recrystallization from benzene-ethanol. The purity of DPH and M-DPH was checked by liquid chromatography. They were identified by IR, UV, and NMR spectroscopies, mass spectrometry and elemental analysis.

Both DPH and M-DPH form spontaneously amorphous glasses via supercooled liquid states when the melt samples are cooled down on standing in air, as characterized by differential scanning calorimetry (DSC) and X-ray diffraction.[5] The glass-transition temperatures of DPH and M-DPH are ca. 50 and 35 °C, respectively. The transparent, amorphous glasses of these materials are very stable, and no crystallization has been noticed for over a year at room temperature for DPH.

Both DPH and M-DPH form transparent films without polymer binders by coating from a solution as well as on cooling from the melt. The films formed by coating from a solution are also found to be amorphous glasses as characterized by DSC and X-ray diffraction. In the present study, the hole drift mobility was measured for the amorphous glassy films prepared by coating from a solution using a glass bar.

Measurements

Hole drift mobilities were measured by a time-of-flight method for a layered device consisting of a charge carrier generation layer (CGL) and a charge carrier transport layer (CTL). A thin film (less than 1 μm) of X-type metal-free phthalocyanine dispersed in polyvinyl butyral is coated on an aluminum substrate to make CGL. A thicker film (10 - 20 μm) of an amorphous glass of DPH or M-DPH as CTL is coated from a methylene chloride solution onto CGL. The solvent was removed at room temperature under vacuum for several hours. Then, a semitransparent gold electrode was vapor deposited on the top of CTL. Hole carriers, photogenerated in CGL upon irradiation of a pulsed white light from a xenon stroboscopic lamp (pulse duration time: 1 - 4 μs), are injected into the CTL sample at time zero and transported across CTL under an external electric field. The photocurrent was monitored using a digital storage scope, KDS-102 (KAWASAKI ELECTRONICA).

RESULTS AND DISCUSSION

As Fig. 1 shows, the transit time (τ_t) was observable in the trace of photocurrent (i_{ph}) as a function of time (t), which was in agreement with the value determined from the plot of log i_{ph} vs log t based on Scher-Montroll theory.[6] The hole drift mobility was calculated from the transit time determined from the plot of log i_{ph} vs log t, according to the expression $\mu = L^2/\tau_t V$, where L is the sample thickness and V the applied voltage. Table 1 lists hole drift mobilities (μ_h) at an electric field of 2.0 x 10^5 V cm^{-1}

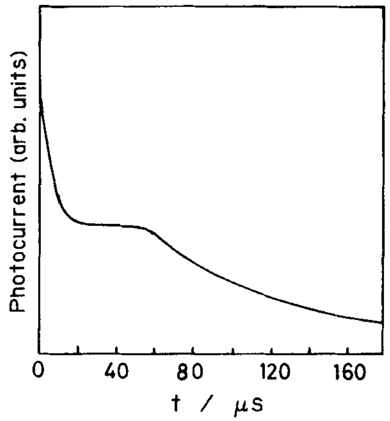


FIGURE 1 Typical transient photocurrent of DPH glass (100%) at 1 x 10^5 V cm^{-1} and at 20 °C.

at 20 °C and the distances (ρ) between molecules determined for 100 % amorphous glasses of DPH and M-DPH, and 50 wt% loaded DPH and M-DPH in polycarbonate. The intersite distance was calculated from the formula $\rho = (M/Ad)^{1/3}$, where M is molecular weight, A Avogadro's number, and d the density. The values of μ_h in the amorphous glassy state of 100 % DPH and M-DPH are found to be more than one order of magnitude greater than those of 50 wt% loaded DPH and M-DPH in polycarbonate under the same conditions.

TABLE I Hole drift mobilities and intersite distances.

	$\mu_h{}^a$ / $cm^2V^{-1}s^{-1}$	ρ / Å
DPH 100 %	2.2×10^{-4}	8.6
DPH 50 wt% in PC	8.7×10^{-6}	10.7
M-DPH 100 %	7.0×10^{-5}	8.7
M-DPH 50 wt% in PC	2.6×10^{-6}	11.0

a) Measured at an electric field of 2.0×10^5 V cm^{-1}, at 20 °C.
PC : polycarbonate.

It has been understood that the drift mobility (μ) in amorphous organic systems is functions of the spacing between molecules (ρ), temperature (T) and electric field (E), and generally expressed by Eq. 1.[2]

$$\mu = \mu_0 \rho^2 \exp[f_1(\rho)]\exp[f_2(T,\rho)]\exp[f_3(E,T,\rho)] \qquad (1)$$

Several models have been proposed to explain temperature and electric-field dependencies of drift mobilities in disordered systems such as doped polymers.[2,7-9] Temperature and electric-field dependencies of the hole drift mobilities of DPH and M-DPH in their glassy states were fit to an empirical equation proposed by Gill (Eq. 2);[7]

$$\mu = \mu_0 \exp[-(E_0 - \beta_{PF}F^{1/2}) / k_B T_{eff}] \qquad (2)$$

$$T_{eff}{}^{-1} = T^{-1} - T_0{}^{-1}$$

where E_0 is the activation energy at the zero electric field, β_{PF} the Pool-Frenkel coefficient, k_B Boltzmann's constant, F electric field, T_0 the temperature at which the extrapolated data of Arrhenius plots at various electric fields intersect with one another, and μ_0 the mobility at T_0.

Figure 2 shows electric-field dependence of the hole drift mobilities of DPH and M-DPH in their glassy films. In the figure, the data for 50 wt% DPH and M-DPH dispersed in polycarbonate are also included for comparison. The results show that the hole drift mobilities of DPH and M-DPH are proportional to $\exp(\beta F^{1/2})$. Figure 3 shows Arrhenius plots of the hole drift mobilities of DPH in its glassy state at different electric fields.

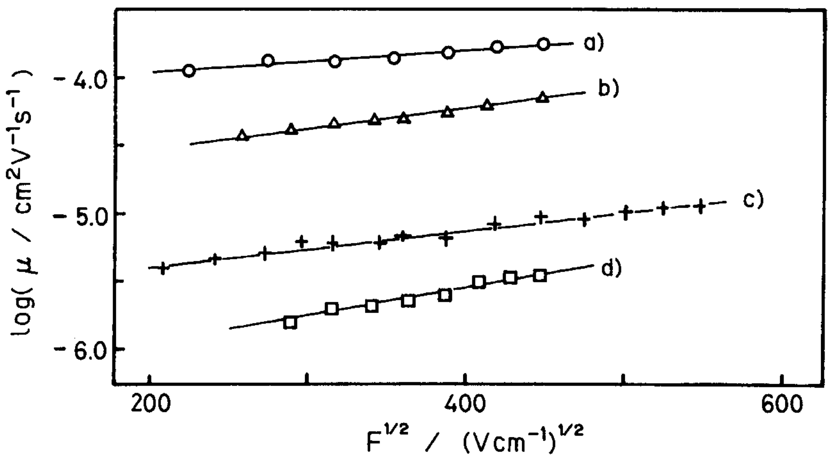


FIGURE 2 Electric-field dependence of hole drift mobilities at 20 °C in the glassy state of a) DPH and b) M-DPH, and c) DPH 50 wt% in polycarbonate (PC) and d) M-DPH 50 wt% in PC.

The activation energy at the zero electric field (E_0) in Eq. 2 was determined by extrapolation of the plot of the activation energy (E_{act}) vs $F^{1/2}$ to the zero electric field, as shown in Fig. 4.

The hole transport parameters, μ_0, E_0 and T_0, in Eq. 2, as evaluated from Figs. 3 and 4, are summarized in TABLE II.

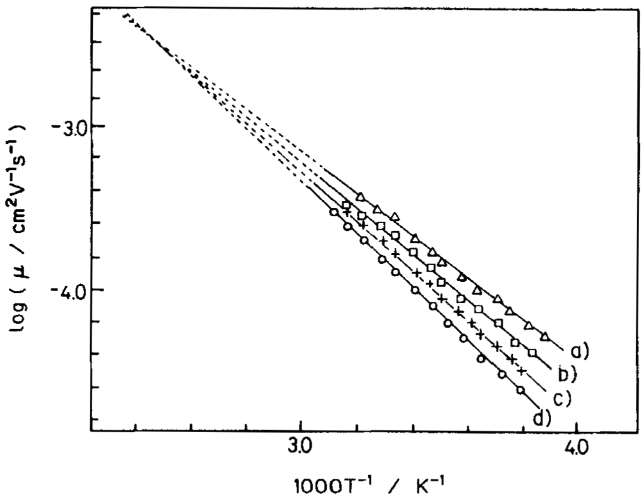


FIGURE 3 Arrhenius plots of the hole drift mobilities of DPH in its glassy state at different electric fields; a) 2.0 x 10^5, b) 1.5 x 10^5, c) 1.0 x 10^5, d) 5.0 x 10^4 V cm^{-1}.

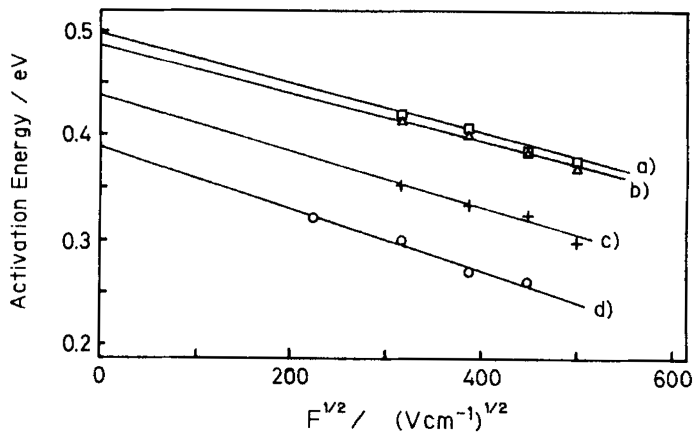


FIGURE 4 Plots of activation energies vs $F^{1/2}$; a) M-DPH 50 wt% in polycarbonate (PC), b) M-DPH 100 %, c) DPH 50 wt% in PC, d) DPH 100 %.

TABLE II Hole transport parameters based on Eq. 2.

		μ_0 / $cm^2V^{-1}s^{-1}$	E_0 / eV	T_0 / K
DPH	100 %	4.2 x 10^{-3}	0.39	420
DPH	50 wt%	3.2 x 10^{-4}	0.44	416
M-DPH	100 %	2.7 x 10^{-3}	0.48	408
M-DPH	50 wt%	1.0 x 10^{-4}	0.50	387

Bässler et al. have proposed a model based on disorder, which considers Gaussian distribution of localized sites due to both energy disorder and disorder of the intersite overlap.[8,9] According to them, temperature and electric-field dependencies of the drift mobility in disordered systems are given by Eq. 3,[9]

$$\mu(E,T) = \mu_0 \exp-(T_0/T)^2 \exp(\beta E^{1/2}) \tag{3}$$

where T_0 is proportional to the Gaussian width σ (T_0/σ = 7400 K eV^{-1}) of the site energy distribution and μ_0 the mobility of a *hypothetical energy disorder-free system extrapolated to* $T \to \infty$.[3,8,9]

The present results were also found to be fit to Eq. 3 as shown from the linear plots of log $\mu(E=0)$ vs T^{-2} in Fig. 5. Hole transport parameters *in* Eq. 3, μ_0, T_0 *and* σ, *are summarized in* TABLE III.

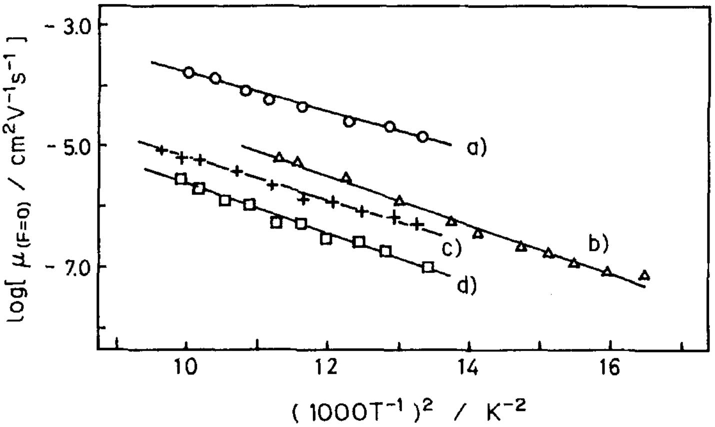


FIGURE 5 Plots of the logarithm of hole drift mobilities at the zero electric field vs T^{-2} a) DPH 100 %, b) DPH 50 wt%, c) M-DPH 100 %, d) M-DPH 50wt%.

TABLE III Hole transport parameters based on Eq. 3.

		μ_0 / $cm^2V^{-1}s^{-1}$	T_0 / K	σ / eV
DPH	100 %	2.1×10^{-1}	849	0.11
DPH	50 wt%	4.5×10^{-2}	878	0.12
M-DPH	100 %	1.1×10^{-1}	937	0.13
M-DPH	50 wt%	1.8×10^{-2}	950	0.13

It has been generally accepted that the transport in disordered systems takes place by a hopping process and that charge transport is an electric-field driven chain of redox processes involving neutral molecules and charged molecules.[1]

Approximately one-order of magnitude higher μ_h and μ_0 together with lower activation energies and smaller distribution width for the amorphous glasses of 100 % DPH and M-DPH than for 50 wt% loaded DPH and M-DPH in polycarbonate may be partly due to shorter spacing of the molecules and less fluctuation of localized hopping sites for the glasses of 100 % DPH and M-DPH than for molecularly doped polymers. Charge transport may be more favorable for the glass of 100 % transporting materials, where interactions exist between the radical cation and the surrounding neutral transporting materials, than for molecularly doped systems, where the charged molecule interacts with the polymer binder, upon which μ is strongly dependent.[3,10]

It is of interest to note that μ_h of the arylaldehyde hydrazone DPH is ca. twice as high as that of the corresponding arylketone hydrazone M-DPH under the same conditions, in spite of the fact that there is no change in the π-electron skeleton. The steric effect by the methyl-substituent in M-DPH might affect the intersite distance and the intermolecular overlap of π-electrons.

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