Charge Transport in the Supercooled Liquid State of Arylaldehyde Hydrazones

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Charge transport in the supercooled liquid state of 4-diphenylamino-benzaldehyde methylphenylhydrazone (Tg=30°C) and 4-diethylamino-benzaldehyde diphenylhydrazone (Tg=8°C) has been studied and compared with that in their molecular glasses. The hole drift mobility of the supercooled liquid state in the temperature region above Tg was smaller than that predicted from the temperature dependence of the hole drift mobility of the glass in the region below Tg. The electric-field and temperature dependencies of the hole drift mobility were analyzed in terms of the disorder formalism.

INTRODUCTION

Charge transport in organic disordered systems, in particular, molecularly-doped polymer systems, has been a subject of recent extensive studies in view of both academic interest and practical application to electro-photography. It has generally been accepted that the charge-carrier drift mobility of organic disordered systems is dependent upon both electric field and temperature and that charge transport in organic disordered systems takes place by a hopping process. A few models have been proposed to explain electric-field and temperature dependencies of charge-carrier drift mobility in organic disordered systems, which include the Poole-Frenkel model,[1] the small polaron model,[2,3] and the disorder formalism.[4,5]

It has recently been revealed that charge transport in molecularly-doped polymer systems, where the binder polymer was thought to be inert for

charge transport, is greatly affected by the binder polymer. In fact, hole drift mobilities of molecularly-doped polymer systems have been reported to vary by two-orders of magnitude depending upon the binder polymer.[6,7]

In order to clarify intrinsic charge-transport properties of low molecular-weight organic disordered systems, it is desirable to investigate charge transport in the amorphous glassy state of low molecular-weight organic materials, namely, molecular glasses. We have found that a series of arylaldehyde and arylketone hydrazones form stable amorphous glasses above room temperature and investigated charge transport in their molecular glasses.[8-11]

It is of interest to investigate charge transport in the supercooled liquid state in comparison with that in the molecular glass. A few studies have been made of charge transport in the supercooled liquid state of molecularly-doped polymer systems[12,13] and a vacuum evaporated film of bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane.[14]

In the present study, we have studied charge transport in the supercooled liquid state of 4-diphenylaminobenzaldehyde methylphenyl-hydrazone (DPMH) with a glass-transition temperature (Tg) of 30°C and 4-diethylaminobenzaldehyde diphenylhydrazone (DEH) with a Tg of 8°C in comparison with that in their molecular glasses. These hydrazone compounds are suitable for studying charge transport in the supercooled liquid state because they show Tgs at around room temperature.
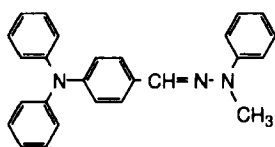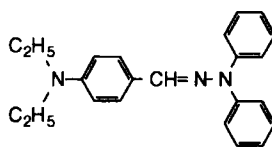
DPMH   DEH

EXPERIMENTAL

Hole drift mobility was measured by the time-of-flight technique using a layered device which consists of a charge-carrier generation layer (CGL) and a charge-carrier transport layer (CTL).[9-11] An appropriate amount of the material was heated to melt on an indium-tin-oxide (ITO)-coated glass. This was pressed by another ITO glass, on which a thin film (thickness: less than 1 μm) of x-type metal-free phthalocyanine was coated by the spin coating method as the CGL. The photocurrent was monitored using a digital storage oscilloscope, TDS 540A (Tektronix). The temperature was controlled by a temperature controller (Oxford ITC 502). The hole drift mobility was

measured in the temperature region from -68°C to 67°C for DPMH and from -73°C to 37°C for DEH.

RESULTS AND DISCUSSION

DPMH and DEH form spontaneously amorphous glasses via supercooled liquid states when the melt samples are cooled on standing in air, as characterized by DSC and X-ray diffraction. When the glass is heated, a glass-transition phenomenon is observed to give the supercooled liquid. The glass-transition temperatures (Tg) of DPMH and DEH are *ca.* 30°C and 8°C, respectively, as measured by DSC.[8,10,11]

The transient photocurrent (i_{ph}) as a function of time (t) for the supercooled liquids of DPMH and DEH exhibited a nondispersive curve. The transit time (τ_t) was determined from the plot of log i_{ph} *vs.* log t based on a Scher-Montroll theory.[15] The hole drift mobility was calculated from the transit time, according to the expression $\mu = L^2/\tau_t V$, where L is the sample thickness and V the applied voltage.

The hole drift mobilities (μ_h) of DPMH and DEH in their supercooled liquid states at an electric field of 1.0×10^5 Vcm^{-1} were determined to be 7.3×10^{-5} (at 67°C) and 1.0×10^{-5} cm^{2}V^{-1}s^{-1} (at 37°C), respectively.

The electric-field and temperature dependencies of the hole drift mobilities of these arylaldehyde hydrazones in their supercooled liquid states as well as the glassy state were analyzed in terms of the disorder formalism, which assumes that charge transport occurs by hopping through a manifold of localized states with superimposed positional disorder and that the distributions of hopping-site energies (diagonal disorder) and distances (off-diagonal disorder) are Gaussian. According to Monté Carlo simulations based on this model, temperature and electric-field dependencies of charge-carrier drift mobility are given by Eq. (1):

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

$$\hat{\sigma} = \frac{\sigma}{kT}$$

where σ is the width of the Gaussian density of states, Σ a parameter that characterizes the degree of positional disorder, μ_0 a hypothetical mobility in the energetic disorder-free system, E the electric field, and C an empirical constant.

As observed for the glassy state, the electric-field dependence of the hole drift mobilities of these hydrazones in their supercooled liquid states at T>Tg was also found to be described by $\exp(\beta E^{1/2})$, as shown in Fig. 1.
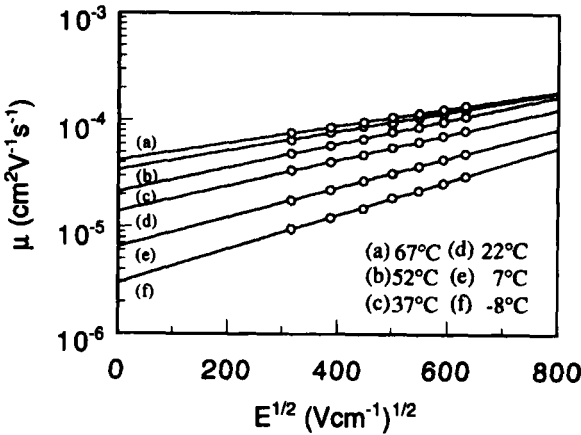
FIGURE 1 Electric-field dependencies of the hole drift
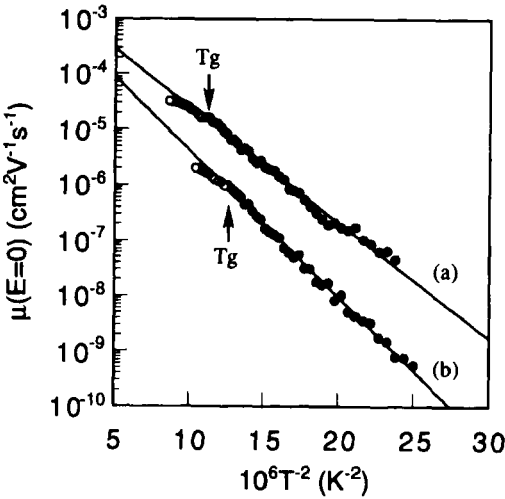mobility of DPMH at various temperatures.

FIGURE 2 Plots of $\mu(E=0)$ *vs.* T^{-2} for (a)DPMH and (b)DEH.

The temperature dependence of the hole drift mobility was analyzed in terms of Eq. (1). Fig. 2 shows the plots of log $\mu(E=0)$ *vs.* T^{-2} for DPMH and DEH over a wide range of temperature encompassing the T_g. The parameters σ and μ_0 for the molecular glass were obtained from the slope of the linear plots in the temperature region below T_g and from the intercept of

the linear plots extrapolated to T→∞, respectively. The charge-transport parameters for the glasses of DPMH and DEH are listed in Table I.

Table I Hole-transport parameters for the molecular glasses of DPMH and DEH

materials	$\mu(E=0)$ / cm^{2}V^{-1}s^{-1}	μ_0 / cm^{2}V^{-1}s^{-1}	σ / eV	Σ	C / (cm/V)$^{1/2}$
DPMH	1.3×10^{-5} [a)]	3.1×10^{-3}	0.090	2.2	3.8×10^{-4}
DEH	6.0×10^{-7} [b)]	1.9×10^{-3}	0.101	2.1	2.7×10^{-4}

a) measured at 20°C, b) measured at 0°C

Fig. 2 clearly shows that the temperature dependence of the hole drift mobility in the region above Tg becomes smaller than that in the region below Tg and that the values of the hole drift mobility determined at T>Tg are smaller than those predicted from the temperature dependence of the hole drift mobility in the region below Tg. That is, the value of the hole drift mobility at the zero-electric field at the temperature higher than Tg by *ca.* 30°C is almost two thirds of the value predicted from the temperature dependence below Tg for both DPMH and DEH. Furthermore, the temperature dependence of the hole drift mobility in the temperature region above Tg is not linear but makes an up-convex curve for these arylaldehyde hydrazones.

Two possibilities are conceivable to explain the smaller hole drift mobility at T>Tg than predicted from the temperature dependence below Tg. One is based on the assumption that μ_0 for the supercooled liquid is different from μ_0 for the glass because of the difference in the magnitude of positional disorder Σ between the two states. If the value obtained by the extrapolation of the up-convex curve to T→∞ is assumed to be μ_0 for the supercooled liquid, then μ_0 for the supercooled liquid is approximately one-order of magnitude smaller than μ_0 for the glass. The decrease in μ_0 on going from the glass to the supercooled liquid stems from the decrease in Σ by a factor of $\exp(\Sigma^2/2)$ in Eq. 2, where the intersite distance ρ is thought to be the same for the two states. On the other hand, σ becomes smaller for the supercooled liquid than that for the glass, which contributes to the increase in the drift mobility.

$$\mu_0 = \mu_{00}\rho^2 \exp\left(\frac{\Sigma^2}{2}\right)\exp\left(-\frac{2\rho}{\rho_0}\right) \qquad (2)$$

The other is based on the assumption that μ_0 is the same for both the glass at T<Tg and the supercooled liquid at T>Tg. Then, the decreased hole drift mobility for the supercooled liquid is ascribed to larger σ for the supercooled liquid than for the glass. In this case, the value σ at each

temperature in the temperature region above Tg is obtained from the slope of the straight line drawn for μ_0 and $\mu(E=0)$ measured at each temperature according to Eq. (3).

$$\sigma(T) = \frac{3}{2}\left[\ln\left(\frac{\mu_0}{\mu(E=0)}\right)\right]^{1/2} kT \qquad (3)$$

SUMMARY

Charge transport in the supercooled liquid state of DPMH and DEH was investigated. The results show that the electric-field dependence of the hole drift mobility follows $\exp(\beta E^{1/2})$ for both the glass and the supercooled liquid and that the values of the hole drift mobility of the supercooled liquid in the temperature region above Tg are smaller than those predicted from the temperature dependence of the hole drift mobility of the glass at T<Tg.

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