

amounts of alcohol (<1%) dissolved in the nonpolar hydrocarbon liquid can more than double the strength of the adhesion force. It is therefore concluded that the polarity of the alcohols present in the white oil is most likely the reason for the extra adhesion. This is consistent with previous findings that trace amounts of both water and methanol can drastically increase the adhesion of mica and other hydrophilic surfaces immersed in various hydrocarbon liquids.<sup>1,4,16,21</sup> The origin of this extra attraction is, however, still not understood.

In the light of the results presented here, it is somewhat clearer as to why isoparaffins, and other branched chain molecules, make good lubricating oils. Branching of hydrocarbon chains, even when limited to only one methyl group, eliminates the layered structure common to symmetric liquids constrained between two surfaces. This prevents the surfaces from coming into contact by the progressive sliding out of molecular layers or from coming into adhesive minima at discrete molecular separations, at which positions there are strong frictional forces on shearing one surface relative to the other.<sup>25</sup> The monotonic repulsion, observed at small surface separations when 2-methyloctadecane, 2-methylundecane, or white oil are the intervening liquids, acts as a soft cushion, which prevents the surfaces from coming too close together thereby averting high friction and surface damage.

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**Registry No.** 2-Methyloctadecane, 1560-88-9; 2-methylundecane, 7045-71-8; 2-methyloctane, 7732-18-5; 1-octanol, 111-87-5.

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## Improved Hole Drift Mobility in Excimer-Free Polymers Containing a Dimeric Carbazole Unit

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**ABSTRACT:** Hole drift mobility of a series of homo- and copolymers containing a dimeric carbazole unit, 1,2-*trans*-bis(9H-carbazol-9-yl)cyclobutane (DCZB), was measured. The hole drift mobility of the polymer containing only the DCZB group as the functional group is more than 10 times higher than that of poly(9-vinylcarbazole) (PVK) or poly(9-ethyl-3-vinylcarbazole) (P3VK). Comparison of their photophysical properties indicated that the high hole drift mobility of the DCZB polymers was brought about by the reduction of the concentration of trapping sites (excimer-forming sites (EFS)). The concentration is much smaller in the DCZB polymers than in PVK or P3VK. This was further confirmed by the temperature and electric field dependence of the mobility.

## Introduction

Interest in charge transport in amorphous organic materials has been increasing in connection with their potential applications as photoreceptor materials in electrophotographic processes such as photocopying and laser printing. Recently, photoreceptors with layered structure consisting of a charge-transport layer (CTL) and a charge-generation layer (CGL) have been most commonly

used. High efficiency of charge transport in CTL is strongly desired to improve the overall sensitivity of the photoreceptor. There are several scientific publications concerning charge transport in organic films.<sup>1-20</sup> However, the detailed mechanism of the charge transport has not been fully understood.<sup>10</sup> For example, there is no widely accepted explanation for the origin of temperature and field dependence of charge mobility or for the relationship

Table I  
Characterization of the Polymers Used in This Study

polymer <sup>a</sup>	$\bar{M}_n^b$	$X^c$	wt % of DCZB <sup>d</sup>	wt % of carbazole <sup>e</sup>	$I_{450}/I_{370}^f$	$T_g^g$ , °C
PVDCZB	$2.5 \times 10^5$	1.00	93.7	81.6	0.05	214
copolymer-67	$3.6 \times 10^5$	0.67	72.9	80.2	0.10	196
copolymer-9	$2.5 \times 10^5$	0.09	14.5	76.6	0.25	190
P3VK	$3.9 \times 10^5$	0.00	0.0	75.7	0.28	191
PVK	$2.0 \times 10^5$		0.0	86.6	1.35	204

<sup>a</sup>For structures of these polymers see Figure 1. <sup>b</sup>Number-average molecular weight determined by gel permeation chromatography, calibrated with standard polystyrenes. <sup>c</sup>Unit content of vinyl (DCZB) determined from gel permeation chromatography and elemental analysis; see ref 24. <sup>d</sup>Calculated for DCZB unit as  $C_{28}H_{22}N_2$ . <sup>e</sup>Calculated for carbazole unit as  $C_{12}H_9N$ . <sup>f</sup>The intensity ratio of excimer (450 nm) to monomer (370 nm) emission for dilute solution in *N,N*-dimethylformamide; see ref 24. <sup>g</sup>Determined from differential scanning calorimetry.

between the mobility and chemical structure of the polymers.

Another unsolved problem is the difference between polymeric hole transport materials and the corresponding monomeric materials dissolved in polymer matrices. Earlier studies were mainly concerned with polymeric materials represented by poly(9-vinylcarbazole) (PVK),<sup>4-6,11-13</sup> while recently solid solutions of active transport molecules in inert polymer have been used more commonly.<sup>7,10,14-16</sup> These solid solution systems have larger freedom in material design and, usually, are superior in charge-transport characteristics compared to polymeric materials.<sup>17</sup> For example, the hole drift mobility ( $\mu$ ) in a PVK film is nearly the same as that of 9-isopropylcarbazole in polycarbonate in spite of the large difference in carbazole group concentration (87 mol % for PVK and 44 mol % for 9-isopropylcarbazole/polycarbonate).<sup>17</sup> Since the mobility in hopping transport increases with the concentration of active groups,<sup>1-3,6</sup> these results clearly show the inferiority of the polymeric charge-transport material. The origin of this negative polymer effect is believed to be the presence of the structural carrier traps in the films.<sup>18,19</sup> If these traps in polymeric transport materials can be removed while maintaining the high concentration of the active groups, the hole drift mobility of polymeric transport materials would be much improved and become larger than that in solid solution systems. On the basis of this assumption, we tried to improve the hole drift mobility of the polymeric transport material by choosing a series of carbazole polymers having different chromophore densities and structures.

It is believed that charge transport and exciton transport have many features in common.<sup>5</sup> Excimer-forming sites (EFS) provide a good model for the structural trapping sites in PVK and other polymers with large aromatic rings.<sup>18,19</sup> The parallel (sandwich type) conformation giving excimer fluorescence is well-known in PVK.<sup>21,22</sup> We have reported that the use of a dimeric carbazole group, *trans*-1,2-bis(9*H*-carbazol-9-yl)cyclobutane (DCZB), instead of a simple carbazole group, reduces the EFS concentration and that photoconductivity determined by the xerographic process (photoinduced decay of the surface charge) is improved for polymers containing DCZB groups.<sup>26,27</sup> However, it is difficult to develop detailed discussion on the hole drift mobility on the basis of xerographic measurement.

Here we report the hole drift mobilities of the DCZB polymers in comparison with that of some other carbazole polymers and copolymers and discuss the hole-transport mechanism in connection with their photophysical properties.

## Experimental Section

**Samples.** Synthesis and characterization of the polymers and copolymers used in the present study were described elsewhere.<sup>23</sup>

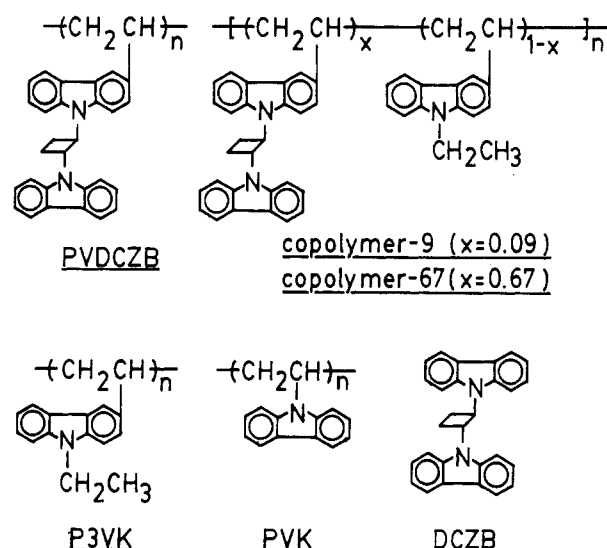


Figure 1. Structures of the materials used in this study.

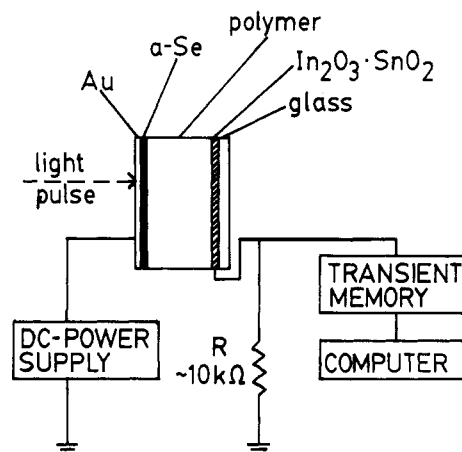
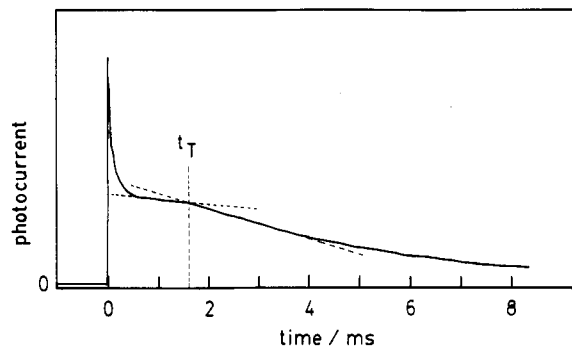


Figure 2. Scheme of the measurement system for time of flight measurements.

Structures and basic properties of these polymers are shown in Figure 1 and Table I, respectively. Films of 3–10- $\mu\text{m}$  thickness for the drift mobility measurements were prepared by casting 1,2-dichloroethane or chlorobenzene solutions of the polymers onto  $\text{SnO}_2$ - $\text{In}_2\text{O}_3$ -coated glass substrates. The films were dried at 60 °C for 24 h under reduced pressure. A thin amorphous selenium (a-Se) layer ( $\sim 0.5 \mu\text{m}$ ) and a semitransparent gold electrode were vacuum deposited successively onto the polymer film, thus we obtained a layered structure (Au/a-Se/polymer/ $\text{SnO}_2$ - $\text{In}_2\text{O}_3$ /glass). Film thickness was determined from the capacitance measurement of the sample film or with a microtopographer (Sloan, Dektak II A).

**Hole Drift Mobility Measurements.** Hole drift mobilities were measured by the time-of-flight method,<sup>28,29</sup> as schematically illustrated in Figure 2. A light pulse of 1- $\mu\text{s}$  width from a xenon flash lamp was introduced to the a-Se layer through the positively



**Figure 3.** Typical transient current signal. Sample, PVDCZB; thickness, 6  $\mu\text{m}$ ; applied field, 0.2 MV/cm; temperature, 25  $^{\circ}\text{C}$ .

biased semitransparent gold electrode. The holes photogenerated in the a-Se layer were injected into and drifted through the polymer layer. The transient current pulse due to hole movement was stored in a digital transient memory (Kawasaki Electronics, M-50E), and the data were transferred to a microcomputer where analysis was performed. During the measurement, the sample was kept in a temperature-controlled chamber equipped with a heater, an inlet and an outlet of  $\text{N}_2$  gas flow, a temperature probe, and a glass window to irradiate the sample. The temperature of the chamber was controlled by a temperature controller above room temperature and by precooled  $\text{N}_2$  gas flow below room temperature. The temperature stability was better than 1 K in the sample mount.

A typical transient current pulse is shown in Figure 3. The transient current shape is very similar to that of PVK and other organic photoconductors.<sup>1,2,6</sup> The time-resolved photocurrent profile is usually characterized as follows.<sup>6,10</sup> An initial sharp pulse is caused by the fast transit of photogenerated holes and electrons in the a-Se layer. After this pulse, there are an almost flat portion and a long tail portion, and both of them are caused by the hole transit in the polymer layer. The demarcation point between the flat and the tail portions is defined as the transit time,  $t_T$ , of the initial sheet of holes.

In most cases, the linear time-current plot was clear enough to determine the demarcation point. However, when the linear plot did not give a clear demarcation point, a double-log plot was used. No appreciable difference in  $t_T$  was observed between these two methods. The hole drift mobility,  $\mu$ , was calculated from the equation  $\mu = d/(t_T F) = d^2/(t_T V)$ , where  $d$  is the sample thickness,  $F$  is the applied electric field, and  $V$  is the applied voltage.

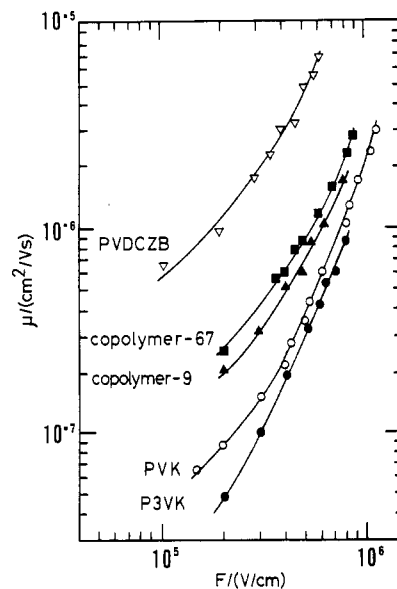
## Results

### Polymer Structure Effects on Hole Drift Mobility.

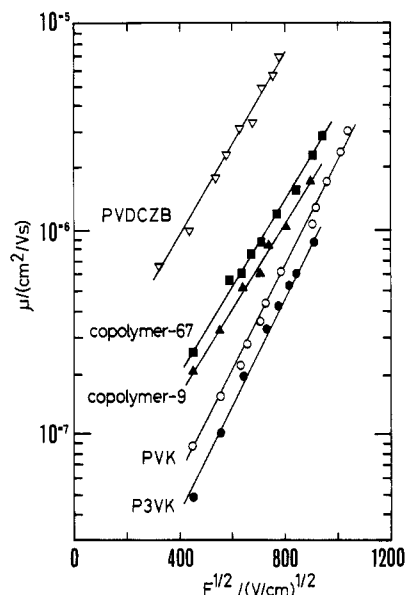
Clear, transparent films of the polymers listed in Table I were prepared easily by conventional solution casting. The thickness of the films was 3–10  $\mu\text{m}$ . The films were tough and stable enough to carry out the mobility measurement up to 1 MV/cm of the applied electric field and in a temperature range between  $-50$  and  $80$   $^{\circ}\text{C}$ . It was very easy to find the bend point corresponding to the transit time and to calculate the hole drift mobility even at low temperatures. Therefore, the lower limit of the electric field was set by the lowering of the photocurrent due to a decrease in the hole mobility.

For all the polymer films studied, the transient current could be observed only when the gold electrode was positively biased, indicating the carrier to be holes and not electrons as already reported for PVK.<sup>6</sup> The hole drift mobility was independent of the film thickness, at least in the range of thickness we studied (3–10  $\mu\text{m}$ ).

Figure 4 shows the hole drift mobility in the polymer films at different applied electric fields at 20  $^{\circ}\text{C}$ . The most important observation is that in spite of the fact that the polymers have the same carbazole unit as the hole-transporting chromophores, their mobilities vary widely depending on their chemical structures. For a given electric field, the mobility of PVDCZB was 10–20 times higher



**Figure 4.** Field dependence of the hole drift mobility of the films of the DCZB and carbazole polymers at 20  $^{\circ}\text{C}$ . A log  $\mu$  versus  $F$  plot.



**Figure 5.** Field dependence of the hole drift mobility of the films of the DCZB and carbazole polymers at 20  $^{\circ}\text{C}$ . A log  $\mu$  versus  $F^{1/2}$  plot.

than that of PVK. The mobility of PVK almost agreed with earlier results.<sup>6,20</sup> Two copolymers showed almost the same mobility at ambient electric field and about twice as high as that of PVK. P3VK showed the lowest mobility. The mobility of P3VK obtained in this study was about 1 order of magnitude higher than that of the earlier result.<sup>20</sup> This discrepancy may arise from different experimental methods and conditions. In the early study, Williams et al. used the xerographic method under space charge limited condition instead of our time-of-flight method under space charge free condition.

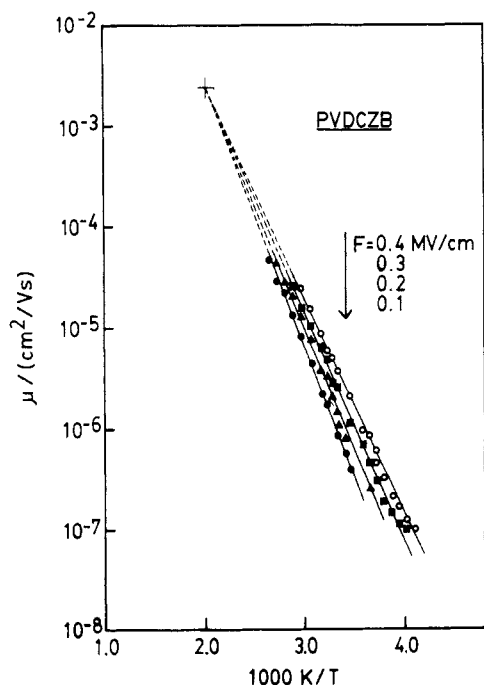
In Figure 5 is shown the plot of log  $\mu$  versus  $F^{1/2}$ . It is clear that the electric field dependence of the mobility in these polymers can be represented by the equation  $\mu(F) \propto \exp F^{1/2}$ .

**Temperature and Electric Field Dependence of Hole Drift Mobility.** Arrhenius plots of the mobility of PVDCZB and P3VK films at different electric fields are shown in Figures 6 and 7, respectively. The plots for the other polymers are essentially the same shape. The data

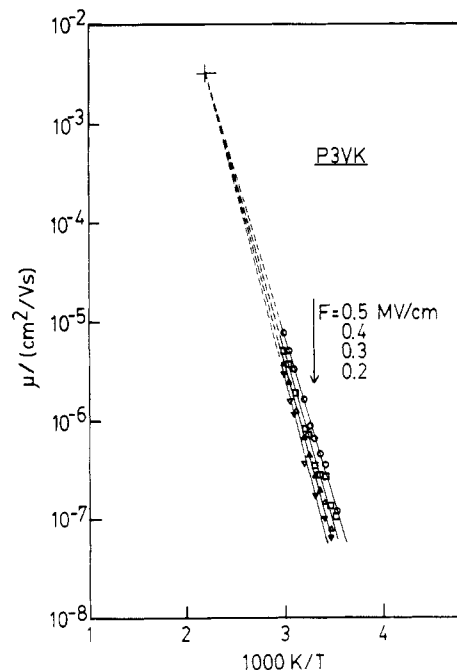
**Table II**  
**Hole Drift Mobilities and the Parameters Obtained by the Temperature Dependence Experiments of the DCZB and Carbazole Polymer Films**

polymer	$\mu^a$ , cm <sup>2</sup> /Vs	$\mu_0^b$ , cm <sup>2</sup> /Vs	$E_0^b$ , eV	$T_0^b$ , °C	$\mu_0^c$ , cm <sup>2</sup> /Vs	$\sigma^c$ , eV
PVDCZB	$3.2 \times 10^{-6}$	$2.4 \times 10^{-3}$	0.62	204	$3.31 \times 10^{-2}$	0.162
copolymer-67	$0.58 \times 10^{-6}$	$2.1 \times 10^{-3}$	0.73	219	$3.47 \times 10^{-2}$	0.175
copolymer-9	$0.49 \times 10^{-6}$	$1.9 \times 10^{-3}$	0.73	217	$2.29 \times 10^{-2}$	0.172
P3VK	$0.19 \times 10^{-6}$	$3.2 \times 10^{-3}$	0.93	181	$18.2 \times 10^{-2}$	0.190
PVK	$0.20 \times 10^{-6}$	$5.5 \times 10^{-3}$	0.65	368	$0.347 \times 10^{-2}$	0.165

<sup>a</sup>Hole drift mobility at 20 °C, 0.4 MV/cm. <sup>b</sup>From Gill's analysis. <sup>c</sup>From Bässler's analysis.



**Figure 6.** Temperature dependence (Arrhenius plot) of the hole drift mobility of a PVDCZB film. Applied electric field as a parameter. The lines correspond to the following equations: for  $F = 0.4$  MV/cm,  $\log \mu = 1.88 - 2150/T$ ; for  $F = 0.3$  MV/cm,  $\log \mu = 2.21 - 2300/T$ ; for  $F = 0.2$  MV/cm,  $\log \mu = 2.62 - 2500/T$ ; for  $F = 0.1$  MV/cm,  $\log \mu = 2.90 - 2640/T$ .



**Figure 7.** Temperature dependence (Arrhenius plot) of the hole drift mobility of a P3VK film. Applied electric field as a parameter. The lines correspond to the following equations: for  $F = 0.5$  MV/cm,  $\log \mu = 4.78 - 3310/T$ ; for  $F = 0.4$  MV/cm,  $\log \mu = 5.17 - 3480/T$ ; for  $F = 0.3$  MV/cm,  $\log \mu = 5.55 - 3650/T$ ; for  $F = 0.2$  MV/cm,  $\log \mu = 5.92 - 3820/T$ .

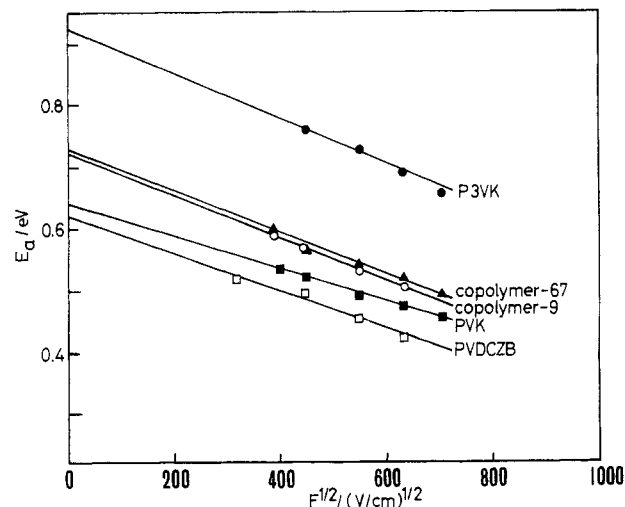
points at each electric field fall on a straight line and the lines for different applied fields cross at a finite temperature. According to Gill,<sup>6</sup> these plots can be analyzed by the following empirical equations:

$$\mu = \mu_0 \exp[-(E_0 - \beta F^{1/2})/kT_{\text{eff}}] \quad (1)$$

$$1/T_{\text{eff}} = 1/T - 1/T_0$$

In these expressions,  $\mu_0$  is the prefactor mobility,  $\beta$  is a constant coefficient,  $k$  is Boltzmann's constant,  $T$  is the film temperature,  $E_0$  is the activation energy extrapolated to zero field, and  $T_0$  is the temperature at which the extrapolated data lines intersect.

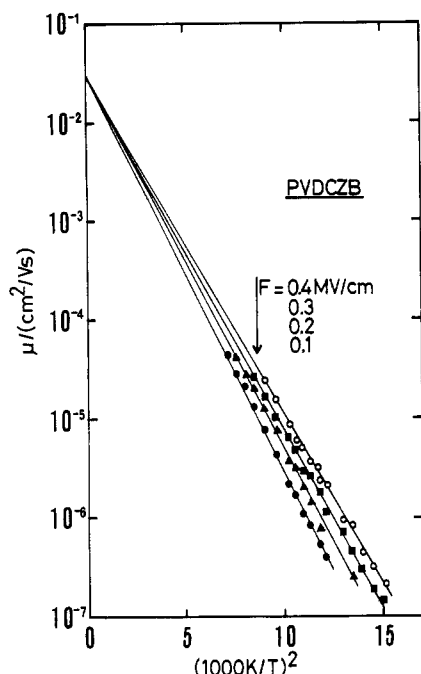
Similar results were obtained for the films of copolymer-67, copolymer-9, and PVK, which were analyzed by eq 1 as well. The parameters,  $\mu_0$ ,  $T_0$ , and  $E_0$  obtained for all the polymers are listed in Table II.  $E_0$  values were obtained by plotting the activation energies at each electric field against the square root of the applied field. As shown in Figure 8, this plot gives a straight line for all polymers, as can be expected from eq 1, and the slope and the intercept correspond to  $\beta$  and  $E_0$ , respectively. As can be seen from Figure 8, the values of  $\beta$  for all the polymers were almost the same, but the values of  $E_0$  of the polymers varied, depending on the structure of the polymer. PVDCZB had the smallest  $E_0$  value and  $E_0$  became larger with increasing content of 9-ethyl-3-vinylcarbazole (3VK)



**Figure 8.**  $E_a$  versus  $F^{1/2}$  plot of the films of the DCZB and carbazole polymers.

moieties in the polymers. The values for  $\mu_0$  and  $T_0$  were scattered to some extent but the differences are not significant, compared with the possible errors arising from their determination.

We tried another method to interpret the temperature and field dependence of the mobility. Recently, Bässler



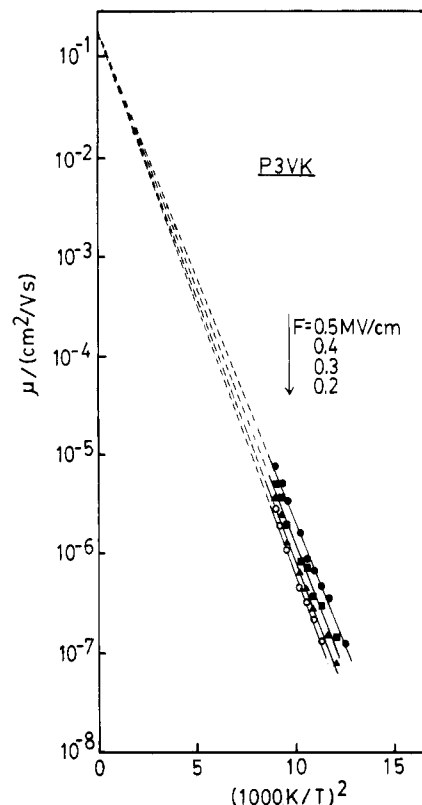
**Figure 9.** Temperature dependence ( $\log \mu$  versus  $1/T^2$  plot) of the hole drift mobility of a PVDCZB film. Applied electric field as a parameter. Each line corresponds to the following equations: for  $F = 0.4$  MV/cm,  $\log \mu = -1.48 - 3.48 \times 10^5/T^2$ ; for  $F = 0.3$  MV/cm,  $\log \mu = -1.48 - 3.64 \times 10^5/T^2$ ; for  $F = 0.2$  MV/cm,  $\log \mu = -1.48 - 3.84 \times 10^5/T^2$ ; for  $F = 0.1$  MV/cm,  $\log \mu = -1.48 - 4.05 \times 10^5/T^2$ .

et al. derived the following equation to explain the temperature and field dependence of the mobility in disordered systems from the simulations of stochastic hopping transport:<sup>3,18,30</sup>

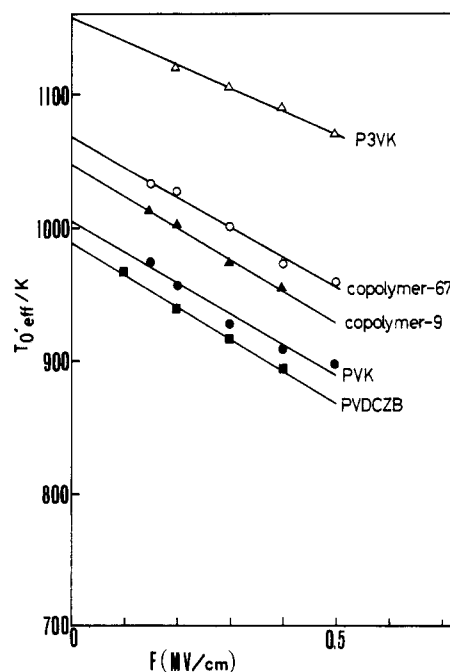
$$\mu(F, T) = \mu_0' \exp[-(T_0'/T)^2] \exp(F/F_0) \quad (2)$$

This equation is based on the assumption that the energy state distribution of the hopping sites is Gaussian and that a carrier initially created energetically at random relaxes during its hopping motion to reach an energy level below the average of available energy states. Since the average value of final energy levels of carriers decreases with temperature, the activation energy of the hopping transport itself will be temperature dependent, with a  $1/T^2$  dependence of the mobility as in eq 2. In eq 2,  $\mu_0'$  represents the mobility when there is no energy distribution of sites,  $T_0'$  is a characteristic temperature related to  $\sigma$ , which is the Gaussian width of distributed hopping site energy, through  $T_0' = 6100 \sigma$ , and  $F_0$  is a parameter defined as  $F_0 = (\sigma/2Be\rho)(T/T_0')^2$ , where  $B$  is a constant reflecting the directions of hopping,  $e$  is the electronic charge, and  $\rho$  is the average of the intersite distance.

If eq 2 holds in our system, a plot of  $\log \mu$  versus  $1/T^2$  should give a straight line for each electric field and these lines should cross each other at  $T \rightarrow \infty$ . Results of the  $\log \mu$  versus  $1/T^2$  plot for PVDCZB and P3VK are shown in Figures 9 and 10, respectively. Again, the data points can be fitted by eq 2 successfully within experimental error. Similar results have been obtained for the other polymers used in this study. Equation 2 predicts that the slopes of the  $\log \mu$  versus  $1/T^2$  plots ( $T_0^{\text{eff}}$ ) are linearly related to the applied field. This relation was in fact confirmed for our system as shown in Figure 11 where  $T_0^{\text{eff}}$ , hence  $\sigma$ , for each polymer was obtained as the intersection at  $F = 0$ . Values of  $\mu_0'$  and  $\sigma$  thus obtained are also listed in Table II. It was found that  $T_0^{\text{eff}}$  increased in the same order as  $E_0$ , namely, PVDCZB < PVK < copolymer-67 < copolymer-9 < P3VK.



**Figure 10.** Temperature dependence ( $\log \mu$  versus  $1/T^2$  plot) of the hole drift mobility of a P3VK film. Applied electric field as a parameter. Each line corresponds to the following equations: for  $F = 0.5$  MV/cm,  $\log \mu = -0.740 - 4.97 \times 10^5/T^2$ ; for  $F = 0.4$  MV/cm,  $\log \mu = -0.740 - 5.16 \times 10^5/T^2$ ; for  $F = 0.3$  MV/cm,  $\log \mu = -0.740 - 5.35 \times 10^5/T^2$ ; for  $F = 0.2$  MV/cm,  $\log \mu = -0.740 - 5.45 \times 10^5/T^2$ .



**Figure 11.**  $T_0^{\text{eff}}$  versus  $F$  plot of the films of the DCZB and carbazole polymers.

## Discussion

Figure 4 illustrates the increase in the hole drift mobility with increasing amount of DCZB group in homopolymers and copolymers of vinyl-DCZB and 3VK. Furthermore, the mobility in PVDCZB is 10–20 times higher than that in PVK. These two results show the superiority of the

DCZB group over the simple carbazole group as a hole-transporting chromophore when they are bonded to the polymer chain. Since photoconduction phenomena in organic solids are believed to be closely related to the photophysical phenomena of the materials,<sup>2-5,19</sup> we discuss here this superiority of the DCZB group in connection with its photophysical characteristics.

Previously, we reported the photophysical properties of the DCZB group and of the polymers containing the DCZB group.<sup>23-25,31</sup> Results are summarized as follows:

1. The absorption spectra of DCZB and DCZB polymers are almost the same as those of 9-ethylcarbazole and PVK.
2. The fluorescence emission spectrum of DCZB is also the same as that of 9-ethylcarbazole both in solutions and in solid solutions in inert polymers. Polymers bearing only the DCZB group show no or very weak fluorescence from the sandwich-type excimer in both solutions and films. This emission behavior of DCZB polymers is one of the most significant differences in comparison with other usual carbazole polymers like PVK or P3VK, whose emissions clearly show the existence of large amount of the sandwich-type excimer.

3. In the cation radical state of the DCZB group, there is some interaction between the two carbazole rings in the DCZB group, as indicated by the fact that their transient absorption spectra are different from those of 9-ethylcarbazole.<sup>31</sup> On the other hand, this type of interaction is negligible in the singlet and triplet excited states and in the anion radical of DCZB, thus the transient absorption spectra are the same as those of 9-ethylcarbazole.

From these photophysical properties of the DCZB group, two explanations for the larger hole drift mobility of PVDCZB are possible. One is the absence of carrier trapping by EFS. The EFS where two carbazole rings have a sandwich-type arrangement is the origin of the excimeric emission of PVK,<sup>21,22</sup> as well as of the carrier trap sites in hole transport in PVK.<sup>3,18,19</sup> PVDCZB is believed to be free of these EFS traps because it shows no sandwich-type excimer emission. As a measure of the concentration of the EFS for the polymers used in this study, Table I includes the value of  $I_e/I_m$ , which is a ratio of the intensity of excimer emission to that of monomer in dilute DMF solutions.

Another explanation is that the hopping site in the DCZB polymers is different from other carbazole polymers. In the DCZB polymers the hopping site could be a whole DCZB group rather than a single carbazole ring because DCZB cation radical is spectroscopically different from an isolated carbazole cation radical. If the hopping motion of holes is faster through the DCZB groups than through the carbazole groups, the DCZB polymers will show a larger hole drift mobility.

It is not clear at the present time which effect is more important in PVDCZB. But, at least, the effect of reduced EFS concentration in the DCZB polymers cannot be ignored since a broad correlation between  $\mu$  and  $I_e/I_m$  values is observed (Tables I and II). Moreover, the latter explanation has some difficulties.

First, the hole drift mobility of DCZB dissolved in polycarbonate is only about twice as high as that of 9-isopropylcarbazole in polycarbonate at the same concentration of carbazole groups.<sup>29</sup> This difference in mobility is not large enough to explain the 10 times difference of mobility between PVDCZB and P3VK.

Second, if the mobility of the polymers is due only to a difference in the rate of hopping motion between DCZB and carbazole groups, the mobility of copolymer-9 seems too large in comparison with P3VK, because it is natural

to suppose that the holes hop mostly through simple carbazole groups in copolymer-9 just like P3VK. On the other hand, the concentration of EFS is more sensitive to chemical structure and, in fact, copolymer-9 exhibits considerably less excimer emission than P3VK, as indicated by the  $I_e/I_m$  values in Table I. This seems to be the reason for the difference in the mobility between copolymer-9 and P3VK.

The ionization potential of the material also affects the hole transport. However, the difference in the ionization potential of the single carbazole group and of the DCZB group is believed to be very small, since the lowest absorption energies of their charge-transfer complexes with 2,4,7-trinitrofluorenone (TNF) are identical.<sup>25,32,33</sup> This is also supported by the fact that a small amount of the DCZB group in copolymer-9 does not act as a hole trap. If the ionization potential of the DCZB group is smaller than that of the carbazole group, a small amount of the DCZB group in copolymer-9 would act as a hole trap.

The temperature and field dependence of the polymers gives us further information on the mechanism of hole transport in the DCZB polymers. The mobilities in all of the present polymers are strongly dependent on both temperature and electric field, as usually observed in other amorphous organic solids, like PVK and PVK-TNF systems.<sup>1-3,6-10</sup> As a result, our data can also be successfully fitted by eq 1 as shown in Figures 6 and 7.

From eq 1, the values of  $E_0$ ,  $T_0$ , and  $\mu_0$  are obtained as the parameters controlling the hole transport. Among these parameters,  $T_0$  and  $\mu_0$  of the polymers are approximately the same. Though  $T_0$  and  $\mu_0$  of P3VK are different from those of the others to some extent, the difference is small if we take into account uncertainty associated with their determination. However,  $E_0$ , the zero field activation energy, has a better accuracy and the values of  $E_0$  of the polymers seem to show the characteristic of their hole transport properly. PVDCZB has the smallest  $E_0$  of 0.62 eV, the two copolymers have the same  $E_0$  of 0.73 eV, and P3VK has the largest  $E_0$  of 0.93 eV. This order is just the order of the mobility itself under a fixed condition.

Sometimes  $E_0$  is regarded as the depth of the hole trap,<sup>19</sup> and in carbazole polymers like PVK, the  $E_0$  value is considered to represent the depth of the hole trap due to EFS. However, at least in the present polymers, it is not appropriate to consider that the  $E_0$  value directly represents the depth of the hole traps due to the EFS. PVDCZB, in which the trapping by EFS is negligible, also has an  $E_0$  value comparable to that of PVK. This  $E_0$  value of PVDCZB must be regarded as the activation energy in the absence of trapping by the EFS, and we will discuss the origin of this activation energy later. Compared to that of PVDCZB,  $E_0$ 's tend to increase with 3VK content in the polymer toward P3VK, and this result can be well explained by the increasing effect of the EFS trapping.

In spite of the large  $\mu$  of PVDCZB, the  $E_0$  value is not much lower than that of PVK. There seem to be shallow hole traps in PVDCZB. One possibility is the presence of a "conformational trap".<sup>34</sup> The charge-transport probability between two carbazole rings with a certain conformation was calculated to be very small.<sup>34</sup> If the rotational movement of the paired carbazole rings is restricted, these pairs might act as a "conformational trap". In PVDCZB, the molecular motion of carbazole groups bonded to a rigid cyclobutane ring will be considerably restricted so that release from a conformational trap seems to require a  $E_0$  value of 0.62 eV.

The analysis of temperature and field dependence of the mobility by Bässler gave almost the same results. In this

analysis, mobility is thought to be affected by  $\sigma$ , the width of the energy distribution of the hopping sites. The values of  $\sigma$  for the present polymers tend to increase with EFS concentration in the polymer film. It can thus be concluded that various EFS's, which act as hopping sites with lower energies than normal carbazole rings, broaden the energy distribution of the hopping sites.

### Conclusion

Hole drift mobility in homo- and copolymers having different DCZB concentrations is measured. The mobility is strongly dependent on the content of the DCZB group in the polymer. The mobility of the polymer containing only the DCZB group, PVDCZB, is much improved and is more than 10 times higher than that of polymers containing no DCZB group, such as PVK or P3VK, in spite of the fact that they have the same carbazole ring as a hole-transporting chromophore.

From the comparison of photophysical properties of the polymers, it is found that the mobility is higher for the polymer that shows less excimer emission. This result can be explained by the decrease in trapping by the EFS due to introduction of the DCZB group, which lowers the EFS concentration.

This is further confirmed by the temperature- and field-dependence measurement of the mobility. The temperature dependence of the mobility is decreased when the concentration of the DCZB group in the polymer is increased, indicating that the influence of trapping by EFS becomes very little.

**Registry No.** PVDCZB (homopolymer), 80218-51-5; (PVDCZB)(P3VK) (copolymer), 80218-52-6; P3VK (homopolymer), 25569-45-3; PVK (homopolymer), 25067-59-8.

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