Hole Transport in Amorphous Films of Poly(*N*-vinylcarbazole), Copolymers of *N*-Vinylcarbazole with Styrene, Polystyrene Molecularly-Doped with *N*-Isopropylcarbazole, and 1,3-Di(*N*-carbazolyl)propane

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ABSTRACT: The hole drift mobility in amorphous films of poly(*N*-vinylcarbazole) prepared by the radical and cationic polymerizations (abbreviated as PVCz(r) and PVCz(c), respectively), copolymers of *N*-vinylcarbazole with styrene (VCz-St), polystyrene molecularly-doped with *N*-isopropylcarbazole (IPCz-PSt), and 1,3-di(*N*-carbazolyl)propane (DCzP(a)) was investigated by the time-of-flight method. The electric field and temperature dependence of the mobility of all the materials fitted the Gill's empirical equation. The mobility of PVCz(r) was larger than that of PVCz(c) by a factor of *ca.* 5—6. By heat-treatment at a temperature above the glass transition temperature, PVCz(r) film was crystallized and its mobility increased by a factor of *ca.* 5. The thermal-crystallization of PVCz(c) film was much more difficult than that of PVCz(r) film and the mobility of PVCz(c) film hardly changed with heat-treatment. These significant differences between PVCz(r) and PVCz(c) seem to be attributable to the difference in their tacticity. The mobility of PVCz(r) increased about twice as much with an increase in the sequence length of VCz chain from 20 to 200, while the mobility of PVCz(c) was independent of it. This may be qualitatively explained by the existence of the chain-end vinyl group in PVCz(r). Under usual conditions ($T=296$ K, $E=1.6 \times 10^5$ V cm^{-1}), the mobility of low molecular-weight compounds (DCzP(a) and IPCz-PSt) was larger than that of polymeric compounds (PVCz and VCz-St). Using the results of a comparison of the values of parameters in the Gill's equation for these films, this was explained by a negative polymer effect due to the higher value of T_0.
KEY WORDS   Drift Mobility / Transient Photocurrent / Photoconduction / Carrier Transport / Poly(*N*-vinylcarbazole) / *N*-Vinylcarbazole Copolymer / 1,3-Di(*N*-carbazolyl)propane / *N*-Isopropylcarbazole /

Considerable interest is being directed to electronic transport in both vinyl aromatic polymers and molecularly-doped polymers from theoretical and practical standpoints. A number of studies have been done on charge transport in poly(*N*-vinylcarbazole) (PVCz), a typical photoconductive polymer,[1-11] and in polycarbonate (PC) films molecularly-doped with *N*-isopropylcarbazole (IPCz) (IPCz-PC)[12,13] or triphenylamine (TPA) (TPA-PC).[13-15] In all these systems, hole drift mobility is described by a hopping mechanism

such that a hole migrates among chromophores in polymeric films or among dopant molecules in molecularly-doped polymers.

On the basis of the NMR spectra and glass transition temperatures of PVCz, we found that samples prepared by the radical polymerization (PVCz(r)) have higher syndiotacticity than those prepared cationically (PVCz(c)).[16] This difference in tacticity between PVCz(r) and PVCz(c) is reflected in the fluorescence spectra both in solution and in films.[17,18] Therefore, it is of interest to investigate how

the difference in the tacticity of PVCz samples is reflected in hole drift mobility. To our knowledge, such an investigation has never hitherto been done.

Epping reported that the photoconductivity of PVCz is independent of the molecular weight in the range from 3×10^5 to 7×10^6.[19] Tanikawa et al. found a photocurrent of PVCz in a surface-type cell to increase with an increase in molecular weight in the range from 1.2×10^3 to 2.4×10^5.[20] However, the effect of molecular weight on hole drift mobility has not hitherto been investigated.

Molecularly-doped polymers are much more flexible in material design since the concentration and kind of dopant molecules and host polymers can be selected from a wide range. Studies on these systems have provided information clarifying the charge transport mechanism. By comparing the hole transport in PC films molecularly-doped with IPCz with that in PVCz films doped with 2,4,7-trinitro-9-fluorenone (TNF),[2] Mort et al. found the vinyl backbone in PVCz not to play a primary role in the transport process but to merely fix the carbazolyl chromophores in space.[12] However, there is no systematic study on polymer effects on hole drift mobility. In such a study, it should be of interest to compare hole drift mobility in PVCz films with that in amorphous neat films of 1,3-di(N-carbazolyl)propane (DCzP(a)), a dimeric model compound of PVCz, since IPCz, a monomeric model compound, does not form an amorphous state except at very low temperatures. It is also important to investigate the hole drift mobility of the copolymer of N-vinylcarbazole (VCz) with a vinyl monomer which is inert in conduction, compared to the mobility in the corresponding molecularly-doped films.

In the present work, we investigated hole drift mobility in PVCz(r) and PVCz(c) films of various molecular weights, copolymer films having various compositions of VCz and styrene (VCz-St), and VCz and vinyl acetate (VCz-VAc), polystyrene films molecularly-doped with IPCz (IPCz-PSt), and DCzP(a).

EXPERIMENTAL

The model compounds (DCzP and IPCz) were the same as those used before.[21] VCz was purified by the usual method from commercial product. A very pure sample of VCz was also synthesized via N-β-chloroethylcarbazole from rigorously-purified carbazole by the procedure described in the synthesis of 5-vinylbenzo[b]-carbazole.[16] The hole drift mobilities of the polymer samples prepared from these two samples of VCz were equal to each other. The PVCz(r) was prepared by polymerization of a 1.3 M benzene solution of purified VCz in the presence of 0.5 mol% AIBN in an evacuated sealed tube at 70°C for 5 h. The PVCz(c) was prepared by polymerization of a 0.074 or 0.31 M toluene solution of purified VCz in the presence of 1 mol% BF_3OEt_2 under a nitrogen atmosphere at 15°C for 1.5 h. The PVCz samples of narrow molecular-weight distribution were prepared by fractional precipitations from their benzene solutions with methanol and purified by reprecipitations three times from benzene solution with methanol. The molecular-weight distribution of the fractions was determined by gel permeation chromatography. Copolymers were prepared by radical copolymerization in a manner similar to that described previously.[22] To obtain copolymers of desired composition, the polymerization yields were limited less than ca. 10%. The VCz content in the copolymers was determined by elementary analysis and/or UV absorption measurements.

The DCzP(a) was prepared in a cell by rapid quenching of the melt, which is sandwiched between nesa-coated and Au-coated conductive quartz plates with a Mylar spacer of 20 μm thick. Polymer films were cast on nesa-coated conductive quartz plates from benzene solutions. A semitransparent gold electrode was evaporated onto a film to prepare a sandwich-type cell. Polymer-film thickness was deter-

mined from the weight and density of a film of known area and/or the capacitive method.

Hole drift mobility was measured with the apparatus described in a previous paper[23] by a conventional time-of-flight method in a vacuum of 2.6×10^{-3} or $1.3\,Pa$. A $3\,\mu s$ light pulse from an air-gap flash was irradiated onto a sample through a narrow interference filter of 340 nm.

RESULTS AND DISCUSSION

The materials used for the present investigation are listed in Table I.

Transient photoresponse was detected only for the illumination of a positively-biased electrode and attributed to hole transport. For both PVCz and the monomeric materials (DCzP(a) and IPCz-PSt), the transit time t_r was determined from a shoulder of the transient response curve. For polymers with a sequence length of VCz chain less than *ca.* 10, no such shoulder could be observed. In such a case, the transit time t_r^* was determined from the bilogarithmic plots based on the theory of Scher and Montroll.[24] The hole drift mobilities calculated from t_r and t_r^* were abbreviated as μ_p and μ_p^*, respectively.

Influence of Tacticity on Hole Drift Mobility

As shown in Figure 1, hole drift mobility is larger for PVCz(r) than for PVCz(c) by a factor of *ca.* 5—6. A probable explanation for this difference in the mobility between PVCz(r) and PVCz(c) may be the trapping effects of the residues of the cationic initiator. This explanation, however, does not account for the fact that the PVCz(r)-2 sample recovered from a benzene solution containing 2.5 mol% of BF_3OEt_2 by the addition of methanol showed

Table I. Material characterization

Sample[a]	M_n	M_w/M_n	μ_{VCz}[b]	$\dfrac{\rho}{Å}$
PVCz(r)-1	195000	2.32	1010	6.47
PVCz(r)-2	116000	1.88	600	6.47
PVCz(r)-3	31100	1.42	160	6.47
PVCz(r)-4	11200	2.10	58	6.47
PVCz(c)-1	791000	—	4100	6.47
PVCz(c)-2	187000	2.63	970	6.47
PVCz(c)-3	40000	2.22	210	6.47
VCz–St(r) (97 mol%)	—	—	32	6.50
VCz–St(r) (83 mol%)	—	—	6	6.71
VCz–St(r) (73 mol%)	—	—	2.7	6.90
VCz–St(r) (50 mol%)	—	—	1.0	7.58
VCz–St(r) (18 mol%)	—	—	0.22	10.1
VCz–St(r) (8.2 mol%)	—	—	0.089	12.9
VCz–VAc(r) (90 mol%)	—	—	10	—
VCz–VAc(r) (80 mol%)	—	—	7.5	—
VCz–St(c) (96.3 mol%)	—	—	26	—
DCzP(a)	—	—	2	6.47
IPCz–PSt (17.5 mol%)	—	—	1	10.3
IPCz–PSt (10.4 mol%)	—	—	1	12.0
IPCz–PSt (6.64 mol%)	—	—	1	13.8

[a] Values in parentheses show VCz and IPCz content.
[b] Average sequence length of VCz chain μ_{VCz} = (fraction of VCz)/(fraction of St) or $\mu_{VCz} = M_n$/(molecular weight of VCz).
[c] Average distance between carbazolyl chromophores in the solid state.

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the same mobility value as observed for the original sample. This difference in mobility thus arises originally from the differences in polymer tacticity.

The electric field and temperature dependences of the mobility of PVCz can be expressed by the Gill's empirical equation:[2]
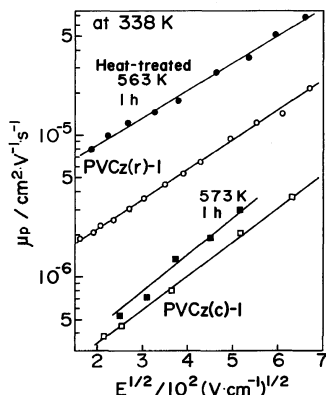

Figure 1. Effects of heat-treatment on the hole drift mobility of PVCz(r)-1 and PVCz(c)-1. PVCz(r)-1: —○—, for untreated film and —●—, for heat-treated film at 563 K for 1 h. PVCz(c)-1: —□—, for untreated film and —■—, for heat-treated film at 573 K for 1 h.

$$\mu_p = \mu_0 \exp\{-(\Delta E_0 - \beta\sqrt{E})/kT_{eff}\} \quad (1)$$

$$1/T_{eff} = 1/T - 1/T_0 \quad (2)$$

where k is the Boltzmann's constant, E, the electric field, T, the film temperature, μ_0, ΔE_0, T_0, and β, the characteristic parameters. The values of the parameters obtained are listed in Table II. The values of T_0 and ΔE_0 for PVCz(c) films were larger than those for PVCz(r) films, while the other values were almost the same for both films. T_0 is the temperature at which the extrapolated temperature dependences at different fields intersect. Above T_0, the Poole-Frenkel type of electric field dependence of the mobility disappears, since the free motion of chromophores destroys some structural traps which prevent hole transport. T_0 is thus related, to a certain extent, to the freezing-in temperature of the segmental motion in amorphous polymer films, that is, the glass transition temperature (T_g).[25,26] The higher value of T_0 results in a lower value of effective temperature (T_{eff}) and, thus, induces smaller mobility. The lower

Table II. Transport parameters[a] and glass transition temperatures

Sample	μ_0 $cm^2 V^{-1} \cdot s^{-1}$	E_0 eV	β $10^{-4} eV/\sqrt{V/cm}$	T_0 K	T_g K
PVCz(r)-1	1.5×10^{-2}	0.54	2.6	725	501
	$*8.5 \times 10^{-3}$	0.53	2.6	730	
PVCz(r)-1[b]	3.2×10^{-2}	0.52	2.6	710	—
	$*2.9 \times 10^{-2}$	0.50	2.2	720	
PVCz(c)-2	1.5×10^{-2}	0.58	2.6	810	518
	$*8.8 \times 10^{-3}$	0.60	2.6	800	
VCz–St(r) (73 mol%)	1.4×10^{-2}	0.56	2.6	730	—
	$*9.0 \times 10^{-3}$	0.56	2.6	720	
VCz–St(r) (50 mol%)	$*5.0 \times 10^{-3}$	0.60	2.8	695	—
VCz–St(r) (8.2 mol%)	$*2.0 \times 10^{-4}$	0.60	2.8	685	386.5
DCzP(a)	7.9×10^{-4}	0.54	3.8	450	303
IPCz–PSt (17.5 mol%)	2.0×10^{-5}	0.40	3.4	455	—
	$*2.5 \times 10^{-5}$	0.44	3.4	450	
IPCz–PSt (10.4 mol%)	3.6×10^{-5}	0.41	2.9	495	—
	$*4.1 \times 10^{-5}$	0.43	2.7	500	
IPCz–PSt (6.64 mol%)	3.2×10^{-5}	0.41	2.4	540	—

[a] * Values were determined from μ_p^*.
[b] Thermally-crystallized film (563 K, 60 min).

drift mobility in PVCz(c) films may possibly be due, in part, to the higher value of T_g.

To further clarify the difference between PVCz(r) and PVCz(c), heat-treatment of polymer films was carried out. Heating of PVCz films on the nesa-coated quartz plates at a temperature above T_g under high vacuum $(1.3 \times 10^{-3}$ Pa) resulted in the appearance of a narrow crystalline X-ray scattering peak at $2\Theta = 8.39°$. This peak indicates the occurrence of paracrystalline lamellar and has been reported both in free-standing films with irregularly stacked lamellar type structures and in films with orderly stacked lamellar structures parallel to roughened aluminum substrates.[27] The values of the peak width at its half height ($\Delta 2\Theta$) of PVCz(r)-1 ($T_g = 501$ K) and PVCz(c)-1 ($T_g = 518$ K) were 0.13° and 0.30° after heat-treatment at 563 K for 60 min and at 600 K for 65 min, respectively. These values did not change with prolonged heat-treatment, and may be regarded as a measure of the dispersion of interchain spacing or of crystal size with average spacing being maintained. The mean dimension of the crystals calculated from the value of $\Delta 2\Theta$ was 75 Å for PVCz(r)-1 and 32 Å for PVCz(c)-1. Under a polarizing microscope, a bright image was observed for the heat-treated sample of PVCz(r)-1. But for the heat-treated sample of PVCz(c)-1, a dark image was observed and growth of a spherulite morphology was not observed. These results indicate that the crystallization of PVCz(c) by heat-treatment is much more difficult than that of PVCz(r).

By heat-treatment, the mobility of PVCz(r)-1 increased by a factor of *ca.* 5, while that of PVCz(c)-1 changed only slightly (Figure 1), indicating the formation of the paracrystalline structure to cause an increase in mobility. The increase in mobility due to crystallization has been reported by Griffiths *et al.* as attributable to an increase in ordering.[28]

The electric field and temperature dependence of the mobility of a thermally-crystallized sample of PVCz(r)-1 was found to follow the

Gill's empirical equation. As listed in Table II, the value of μ_0 increases remarkably, but the value of ΔE_a $(= \Delta E_0 - \beta\sqrt{E})$ decreases slightly with heat-treatment.

Both PVCz(r) and PVCz(c) consist of syndiotactic and isotactic stereoblock structures. PVCz(c) has an isotactic sequence of 50% and PVCz(r), 25%.[16] PVCz(c) has more kinks at joints between isotactic and syndiotactic sequences. The T_g of PVCz(c) is higher than that of PVCz(r). Judging from the polymerization conditions, the characteristics of PVCz in this experiment are quite similar to those described above.

The difficulty in the thermal crystallization of PVCz(c) may arise from differences in tacticity; that is, PVCz(c) has more kinks than PVCz(r).

Traps controlling hole transport in PVCz may possibly derive from structural defects. The kinks may act as traps, since separation between carbazolyl chromophores about the kinks is larger than that in usual sequences. Each trap has a barrier height corresponding to the difference in distance between carbazolyl chromophores. Therefore, the difference in ΔE_a between PVCz(r) and PVCz(c) may possibly be due to differences in the distribution of these barriers in both polymers.

Thermal crystallization caused a slight increase in the density of a PVCz(r) film as a result of a decrease in both the distance between carbazolyl chromophores of neighboring chains and that between those about the kinks. This leads to increased mobility and is another reason for the increase in mobility by the thermal crystallization of PVCz(r)-1.

It has been pointed out that excimer-forming sites may act as traps in the trap-limited hopping process in PVCz.[29] The concentration of excimer-forming sites was greater for PVCz(c) than for PVCz(r) by a factor of *ca.* 1.1—1.2.[18] But this small difference between PVCz(r) and PVCz(c) should not cause the large difference in the mobility of these polymers.

Table III. Effects of doping on hole drift mobility[a]

Sample	μ_p	Dopant[b]	μ_p'	μ_p'/μ_p	Measurement condition
	$cm^2 V^{-1} s^{-1}$		$cm^2 V^{-1} s^{-1}$		
IPCz–PSt (16.7 mol%)	3.0×10^{-6}	TPA (0.037)	2.0×10^{-8}	0.0067	c
DCzP(a)	$*1.9 \times 10^{-6}$	TPA (0.034)	$*1.7 \times 10^{-7}$	0.089	d
PVCz(r)-2	$(6.15 \pm 0.98) \times 10^{-6}$	TPA (0.027)	7.0×10^{-6}	1.1	e
IPCz–PSt (20.2 mol%)	4.5×10^{-6}	VCz (0.054)	1.5×10^{-6}	0.30	c
PVCz(r)-2	$(6.15 \pm 0.98) \times 10^{-6}$	VCz (0.021)	5.4×10^{-6}	0.88	e

[a] *, Values were determined from t_r^*. μ_p, mobility in undoped film; μ_p', mobility in doped film.
[b] TPA, Triphenylamine; VCz, N-Vinylcarbazole. Values in parentheses show molar ratio to carbazolyl chromophores.
[c] $E = 5 \times 10^5 \, V \, cm^{-1}$; $T = 296 \, K$.
[d] $E = 9 \times 10^4 \, V \, cm^{-1}$; $T = 296 \, K$.
[e] $E = 1.6 \times 10^5 \, V \, cm^{-1}$; $T = 338 \, K$.

Doping Effects on Hole Drift Mobility

The addition of a slight amount of TPA into IPCz-PC films has been shown to remarkably reduce hole drift mobility, because TPA has a lower ionization potential than IPCz and acts as a trap.[13] Table III lists the results of doping on hole drift mobility. The mobility in an IPCz-PSt film was reduced remarkably with the addition of a slight amount of TPA. The mobility in a DCzP(a) film was also reduced by the doping of TPA. Although the doping of TPA into a PVCz(r)-2 film made it slightly difficult to observe the shoulder of the transient response curve, it did not reduce the mobility. The doping of VCz into an IPCz-PSt film reduced the mobility to *ca.* 1/3 of its original value, while the doping of VCz into a PVCz(r)-2 hardly reduced the mobility and caused no change in the shape of the transient response curve. This result concerning the mobility is similar to the case of the doping of TPA. PSt films molecularly-doped with VCz (18.4 mol%) showed no photoresponse, although PC films molecularly-doped with TPA were photoconductive.[13–15] Therefore, the reason why VCz acts as a trap is considered to be that localization of a positive charge on the vinyl group of VCz molecule reduces significantly the π-electronic interaction between neighboring carbazolyl chromophores.

It was noted that even a molecule acting as a trap in the low molecular-weight compound (DCzP(a) and IPCz-PSt) system does not do so in neat PVCz film unless the amount of dopant is high. Since the concentration of dopants is low and N-ethylcarbazole is known to be uniformly dispersed in PVCz films even at concentrations up to 30 mol%,[10] dopant molecules seem not to segregate in PVCz films. Sites where dopant molecules do not act effectively as traps may thus exist in neat PVCz film. It may be possible that the sites are in regular arrangement of carbazolyl chromophores along the polymer chain. That is, it is suggested that holes migrate through carbazoyl chromophores along a polymer chain.

Effects of the Sequence Length of VCz Chain on Hole Drift Mobility

In Figure 2, the mobility of PVCz(r) increases to about twice as much with an increase in the squence length of VCz chain from 20 to 200 and levels off to a constant value, while that of PVCz(c) is independent of the sequence length.

Reucroft and Takahashi found the presence of deep hole traps whose density was one trap for every 10^5—10^6 polymer molecules or every 10^8—10^9 monomer units and suggest that the polymer-chain end is not a deep trap.[4] How-
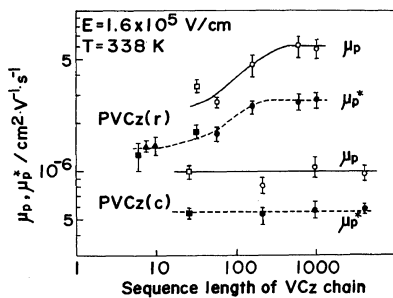
Figure 2. Dependence of hole drift mobility on the sequence length of N-vinylcarbazole chain. ○, ●, PVCz(r), PVCz(c); □, ■, VCz-St copolymer; ▲, VCz-VAc copolymer.
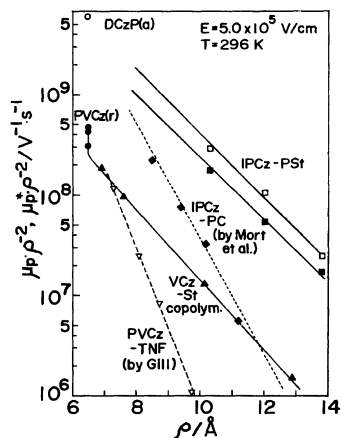

Figure 3. Hole drift mobility plotted as a function of the average distance between carbazolyl chromophores. ●, PVCz(r), ▲, VCz-St copolymer; □, ■, IPCz-PSt, ○, DCzP(a), ▽; PVCz-TNF (by Gill); ◆, IPCz-PC (by Mort *et al.*). Open and closed symbols show μ_p/ρ^2 and μ_p^*/ρ^2, respectively.
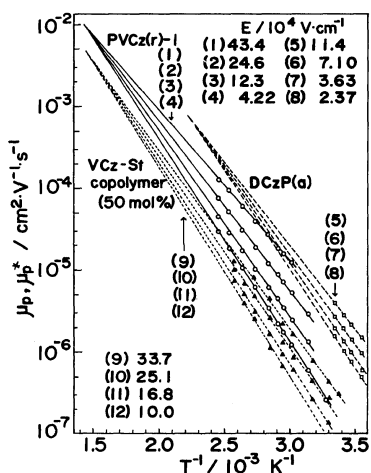

Figure 4. Dependence of hole drift mobility on temperature with the electric field as a parameter.

ever, densities of shallow traps which determine hole mobility, have not been reported.[4] In the case of PVCz(c), judging from the fact that its mobility is constant when the sequence length of VCz chain is greater than *ca.* 26, a hole migrates through carbazolyl chromophores less than *ca.* 26 along a polymer chain and hops to a carbazolyl chromophore belonging to another polymer chain. Because PVCz(r) has fewer kinks than PVCz(c), the number of carbazolyl chromophores through which a hole can migrates along a polymer chain may be larger for PVCz(r) than for PVCz(c).

From the results of doping effects, molecules similar to TPA and VCz incorporated into a PVCz chain should act as traps for holes migrating along the polymer chain. If a termination reaction of the radical polymerization occurs by a disproportionation, PVCz(r) has vinyl groups at a chain end, whose number is inversely proportional to the sequence length of the VCz chain, but PVCz(c) has no such groups. The dependence of mobility on the sequence length of the VCz chain in PVCz(r) seems qualitatively explainable by the existence of chain-end vinyl groups.

Polymer Effects on Hole Drift Mobility

Figure 3 shows the dependence of hole mobility on the average distance between carbazolyl chromophores, ρ, calculated assuming

IPCz molecules to be uniformly dispersed in PSt films and carbazolyl chromophores in copolymers also to be uniformly dispersed. This figure includes both PVCz-TNF charge transfer complex[2] and IPCz-PC systems.[12] Under usual conditions ($T=296$ K, $E=1.6 \times 10^5$ V cm^{-1}), the mobility of low molecular-weight compounds (DCzP(a) and IPCz-PSt) was larger than that of polymeric compounds
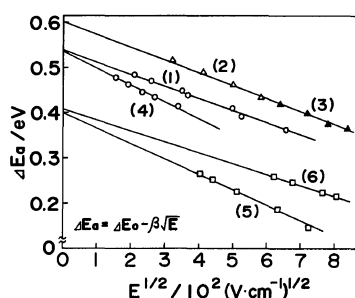
Figure 5. Dependence of activation energy ΔE_a on the electric field. (1), PVCz(r)-1; (2) and (3), VCz-St copolymer (50 mol%) and (8.2 mol%); (4), DCzP(a); (5) and (6), IPCz-PSt (17.5 mol%) and (6.64 mol%).

(PVCz and VCz-St).

The electric field and temperature dependence of the hole drift mobility of all materials investigated fit the Gill's empirical equation 1, as shown in Figures 4 and 5. The values of the parameters obtained are listed in Table II. Remarkable differences in parameters between low molecular-weight and polymeric compounds were found in μ_0, T_0, and ΔE_a. Both T_0 and ΔE_a were lower for low molecular-weight than polymeric compounds. Since these low values lead to high mobility values, the differences in mobility observed in Figure 3 are due to the differences in both T_0 and ΔE_a.

The extrapolated temperature dependences of the mobility at different electric fields intersect at T_0, and thus, samples having low T_0 values tend to have low μ_0 value. This shows that the values of μ_0 and T_0 are not necessarily independent of each other.

In the molecularly-doped system, T_0 decreased with increased content of IPCz. The T_g of these films decreased also with an increase in IPCz content because of the plasticization effect of the dopant molecules. Although the value of T_g, 386.2 K, for VCz-St(r) (8.2 mol%) was close to that of T_g for PSt (377.0 K), the value of T_0 for this copolymer was much larger than those for the molecularly-doped films and close to that for PVCz. These results suggest that T_0 is related not to the freezing-in temperature of the segmental motion around hopping sites, but to the freezing-in temperature of the motion of chromophores which are hopping sites themselves. Such motion promotes the transport.

The above-described results and discussion indicate that the vinyl backbones of polymers do not only fix carbazolyl chromophores in space, as reported by Mort et al.,[12] but also disturb the certain chromophore motions which promote hole transport. The latter is a kind of negative polymer effect.

For phonon-assisted hopping, drift mobility can be expressed as,

$$\mu_p \propto \rho^2 \exp(-2\rho/\rho_0) \qquad (3)$$

where ρ_0 is a measure of the localization of the charge at the hopping site (localization radius). As shown in Figure 3, the experimental results are consistent with eq. 3, and support a transport mechanism involving random hopping among carbazolyl chromophores over the range of concentration. From the slopes of the straight lines in the semilog plot, the localization radius ρ_0 was obtained as 2.5 Å for both molecularly-doped film and copolymer film systems. This means that spatial decay of the electronic wave function is independent of whether the system is polymeric or monomeric.

The value of 2.5 Å is larger than 1.1 or 1.54 Å for PVCz-TNF and IPCz-PC, respectively. The electronic wave function spreads to a greater extent throughout non-polar host materials than polar ones. In Figure 3, the values of μ_p/ρ^2 for two different molecularly-doped systems, IPCz-PSt and IPCz-PC, approach the value for DCzP(a) with an increase in IPCz content. In consideration of hole drift mobility, therefore, non-polar polymers as host materials should be used in molecularly-doped systems.

REFERENCES

1. D. M. Pai, *J. Chem. Phys.*, **52**, 2285 (1970).
2. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
3. J. Mort, *Phys. Rev. B*, **5**, 3329 (1972).

4. P. J. Reucroft and K. Takahashi, *J. Non-Cryst. Solids*, **17**, 71 (1975).
5. M. Ohnishi, *Jpn. J. Appl. Phys.*, **16**, 1717 (1977).
6. C. H. Griffiths, K. Okumura, and A. Van Laeken, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1627 (1977).
7. G. Pfister and C. H. Griffiths, *Phys. Rev. Lett.*, **40**, 659 (1978).
8. B. Reimer and H. Bässler, *Phys. Status Solidi A*, **51**, 445 (1979).
9. M. Yamamoto, T. Hamano, K. Yubakami, N. Tsutsumi, and Y. Nishijima, *Rep. Prog. Polym. Phys. Jpn.*, **23**, 559 (1980).
10. N. Tsutsumi, M. Yamamoto, and Y. Nishijima, *Rep. Prog. Polym. Phys. Jpn.*, **24**, 399 (1981).
11. M. Fujino, H. Mikawa, and M. Yokoyama, *Photogr. Sci. Eng.*, **26**, 84 (1982).
12. J. Mort, G. Pfister, and S. Grammatica, *Solid State Commun.*, **18**, 693 (1976).
13. G. Pfister, S. Grammatica, and J. Mort, *Phys. Rev. Lett.*, **37**, 1360 (1976).
14. G. Pfister, *Phys. Rev. B*, **16**, 3676 (1977).
15. P. M. Borsenberger, W. Mey, and A. Chowdry, *J. Appl. Phys.*, **49**, 273 (1978).
16. K. Okamoto, M. Yamada, A. Itaya, T. Kimura, and S. Kusabayashi, *Macromolecules*, **9**, 645 (1976).
17. A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976).
18. A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 22 (1977).
19. R. H. Epping, "Curr. Probl. Electrophotography," Eur. Colloq., 3rd ed, Walter de Gruyter, 1971 (*Chem. Abstr.*, **80**, 114751c), p 215.
20. K. Tanikawa, T. Enomoto, M. Hatano, K. Moteji, and Z. Okuno, *Makromol. Chem.*, **176**, 3025 (1975).
21. A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Lett.*, 131 (1978).
22. K. Okamoto, K. Kato, K. Murao, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2883 (1973).
23. K. Okamoto and A. Itaya, *Bull. Chem. Soc. Jpn.*, **57**, 1626 (1984).
24. H. Scher and E. W. Montroll, *Phys. Rev. B*, **12**, 2455 (1975).
25. H. Kitayama, M. Yokoyama, and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **76**, 19 (1981).
26. M. Fujino, K. Kanazawa, H. Mikawa, M. Yokoyama, and S. Kusabayashi, *Polym. Prepr. Jpn.*, **32**, 516 (1983).
27. C. H. Griffiths, *Characterization of Metal and Polymer Surfaces*, **2**, 333 (1977).
28. C. H. Griffiths, G. Pfister, and A. Ledwith, "Electronic Properties of Polymers," J. Mort and G. Pfister, Eds., Wiley-Interscience, New York, 1982, p 241.
29. M. Yokoyama, Y. Fukui, and H. Mikawa, *Polym. Prepr. Jpn.*, **31**, 2855 (1982).