The Pulse-photoconductivity of Poly(*N*-vinylbenzocarbazole)s

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The hole-drift mobility and the carrier-photogeneration efficiency of holes in poly(5-vinylbenzo[*b*]carbazole)(P5VBCz) and poly(7-vinylbenzo[*c*]carbazole)(P7VBCz) films were investigated by means of the time-of-flight method and compared with those in poly(*N*-vinylcarbazole)(PVCz) films. The mobilities of these polymers were nearly equal to each other and smaller than that of PVCz by a factor of *ca.* 1/3. The electric field and temperature dependence of the mobilities fit Gill's empirical equation. The small mobilities of both P5VBCz and P7VBCz were apparently attributable to the small values of the pre-exponential factor, μ_0. The carrier-photogeneration efficiencies, ϕ, of these polymers were larger than that of PVCz by a factor of *ca.* 10. The field dependence of ϕ of these polymers for the excitation of the ^1B_a absorption band was in good agreement with the Onsager theory of geminate recombination. These results indicate that the introduction of bulky and unsymmetric benzocarbazolyl chromophores instead of carbazolyl ones as a pendant group of vinyl polymers is a good modification from the point of view of the carrier-photogeneration, but not from the viewpoint of the carrier transport.

There have been many investigations concerning the electrical conductivity of vinyl polymers with large pendant aromatic groups. Considerable data on the photoconductivity of poly(*N*-vinylcarbazole) (PVCz) have been accumulated because of an interest in highly photoconductive polymers.[1—21)] The high photoconductivity of PVCz has been reported to be attributable to both the high efficiency of carrier generation and the ease of carrier migration. The extrinsic carrier-photogeneration *via* nonrelaxed exciplexes has been reported to be predominant for all the excitation bands.[14,20)] The hole-drift mobility is described by a hopping mechanism where a hole migrates among pendant chromophores of polymer chains. Therefore, it is of interest to investigate the photoconductivity of vinyl polymers with aromatic chromophores which are more bulky than a carbazolyl chromophore. We have synthesized poly(5-vinylbenzo[*b*]carbazole)(P5VBCz) and poly(7-vinylbenzo[*c*]carbazole)(P7VBCz).[22)] The stereoregularity of these polymers depends on the polymerization method. They show the excimer fluorescence, while the monomeric compounds, both 5-ethylbenzo[*b*]carbazole and 7-ethylbenzo[*c*]carbazole (7EBCz), show no excimer fluorescence in concentrated solutions. This behavior is very similar to that of PVCz.[22,23)]

In the present paper, the pulse photoconductivity of P5VBCz and P7VBCz has been investigated in comparison with that of PVCz.

Experimental

The P5VBCz was prepared by the bulk polymerization of purified 5-vinylbenzo[*b*]carbazole in the presence of 2 mol% AIBN in an evacuated sealed tube at 100—105 °C for 68 h.[22)] The P7VBCz was prepared by the polymerization of a 0.62 M (1 M=1 mol dm^{-3}) benzene solution of purified 7-vinylbenzo[*c*]carbazole in the presence of 1 mol% AIBN in an evacuated sealed tube at 63 °C for 7 h.[22)] The polymers were reprecipitated three times from the 1,2-dichloroethane solution with methanol. The polymer samples were stored in tubes within an argon atmosphere in the dark. Gel-permeation chromatography analysis showed M_n=2.02×10^4 and M_w/M_n=3.63, and M_n=4.72×10^4 and M_w/M_n=3.35, for P5VBCz and P7VBCz respectively. Films were cast on NESA-coated quartz plates from a 1,2-dichloroethane solution and were dried *in vacuo*. A semitransparent gold electrode with a typical area of 1 cm^2 was evaporated on a film to prepare a sandwich-type cell. The film thickness was determined to be 4.3—7.2 μm from the weight and density of a film with a certain known area and/or by a capacitive method. The densities of the films were 1.21 and 1.22 g cm^{-3} for P5VBCz and P7VBCz respectively. The dielectric constants, ε, of P5VBCz and P7VBCz films were determined to be 3.61 and 3.66 respectively from capacitance measurements at the frequency of 1 kHz at 298 K.

The hole-drift mobility and the carrier-photogeneration efficiency of holes were measured with the apparatus described in a previous paper by means of a conventional time-of-flight method in a vacuum of 2.6×10^{-3} Pa.[20,21)] A 3 μs light pulse from an air-gap flash was irradiated onto a sample through appropriate narrow band-pass filters. The cautions described in a previous paper[20)] were taken in all the procedures in order to get reproducible results.

Results and Discussion

Hole-drift Mobility. For both P5VBCz and P7VBCz, a transient photoresponse was detected only for the illumination of a positively-biased electrode and was attributed to hole transport. It has been reported that PVCz samples with a sequence length of the *N*-vinylcarbazole(VCz) chain of more than *ca.* 10 showed a shoulder of the transient response

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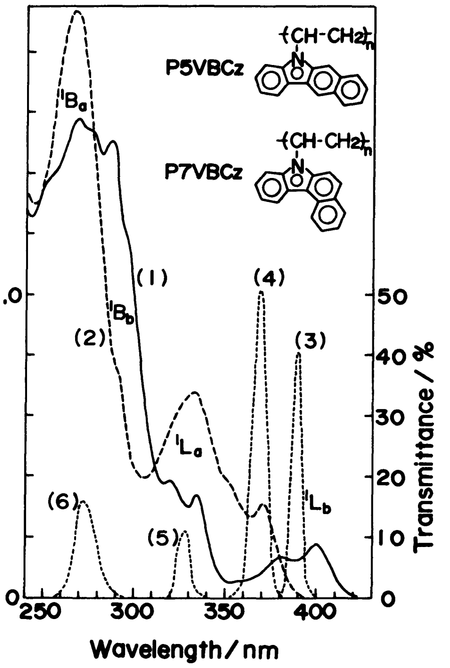

Fig. 1. Absorption spectra of P5VBCz($\approx$0.12 μm thick) (1) and P7VBCz($\approx$0.19 μm thick) (2) films, and transmittance of band-pass filters ((3)—(6)).

curve.[21] For a P5VBCz sample with a degree the polymerization($\overline{DP}$) of 80, such a shoulder was observed, and the transit time, t_r, was determined from it. For a P7VBCz sample of $\overline{DP}$=180, however, no such shoulder was observed except above 363 K. When no shoulder of the transient response curve was observed, 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.

Figure 1 shows the absorption spectra of P5VBCz and P7VBCz thin films and the transmittance of the band-pass filters used. The hole-drift mobility was independent of the excitation bands of ^1L_b, ^1L_a, and ^1B_a. The results mentioned below concerning the hole mobility were obtained by the excitation of ^1B_a and ^1L_a absorption bands for P5VBCz and P7VBCz respectively.

The hole-drift mobilities for both polymers depended strongly on both the electric field and the temperature, as is the case with PVCz.[4,12,16,21] Figure 2 shows the electric-field dependence of the hole mobilities of both polymers at *ca.* 339 K. The result for a PVCz sample of $\overline{DP}$=1010 is also shown for the sake of comparison. Straight lines of log μ against the square root of the electric field show that the Poole-Frenkel-type relation holds for these polymers. Under this condition, the hole mobilities of P5VBCz and P7VBCz were nearly equal to each other and about one-thirds as large as that of PVCz. This is not attributable to the difference of the $\overline{DP}$ values, because the mobilities of the PVCz samples prepared by the radical polymerization were reduced by a factor of only two with a decrease in $\overline{DP}$ from 200 to 20.[21]

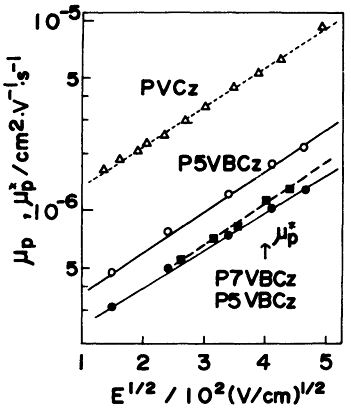

Fig. 2. Field dependence of the hole drift mobility at 339 K.
○,●: P5VBCz, λ_{ex}=270 nm, ■: P7VBCz, λ_{ex}=370 nm, △: PVCz, λ_{ex}=340 nm.

The electric-field and temperature dependence of the hole mobility of PVCz is expressed by Gill's empirical equation:[4]

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

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

where k is the Boltzmann constant; E, the electric field; T, the film temperature, and μ_0, ΔE_0, T_0, and β, the characteristic parameters. We have previously reported that the dependence of the mobilities of the copolymers of VCz with styrene(VCz-St copolymer) on both the electric field and the temperature also fit Gill's empirical equation.[21] Figure 3 shows the temperature dependence of the mobilities of P5VBCz and PVCz under various electric fields. The electric-field dependence of the activation energies, ΔE_a, of P5VBCz, P7VBCz, and PVCz is shown in Fig. 4. These figures indicate that the mobilities of the benzocarbazolyl polymers also follow Gill's equation, as is the case with carbazolyl polymers. The values of the parameters obtained are listed in Table 1. There was a remarkable difference in the parameter, T_0, between carbazolyl and benzocarbazolyl polymers. The glass-transition temperatures of P5VBCz and P7VBCz were higher than that of PVCz, while the T_0 values of the benzocarbazolyl polymers were much lower than those of PVCz and VCz copolymers. The T_0 values of the benzocarbazolyl polymers were close to those of polycarbonate molecularly-doped with 7EBCz (522—405 K) reported by Tsutsumi *et al.*[25] It has been suggested that T_0 was related to the freezing-in temperature of the micro motion of chromophores themselves acting as hopping sites;[21,26] their micro motion destroys some structural traps preventing the hole transport and promotes the transport. It has been suggested that the traps which control the hole transport may be derived from structural defects such as kinks existing at joints between isotactic and syndiotactic sequences.[21] Both P5VBCz and P7VBCz consist of a syndiotactic and isotactic stereoblock structure, as is the case with PVCz.[22] Although both benzo[*b*]carbazole and benzo[*c*]carbazole are bulky compared with carbazole, they both have unsymmetric molecular structure, unlike carbazole. Therefore, the packing between chromophores around the kinks in P5VBCz and P7VBCz may be loose and the chromophores may tend to move to destroy the structural traps at low temperatures as compared with carbazolyl chromophores in PVCz.

The μ_0 values of P5VBCz and P7VBCz were much smaller than that of PVCz, as is shown in Table 1. The μ_0 value of poly(1-vinylpyrene) was close to those of P5VBCz and P7VBCz and much smaller than that of PVCz.[27] Even if a sample with a high value of T_0 tends to have a high value of μ_0, the μ_0 value of PVCz is extremely high. It has been reported that the μ_0 value is related to molecular interaction between chromophores acting as hopping sites[4] and corresponds to the trap-free drift mobility.[19] Therefore, the molecular interaction between carbazolyl chromophores in PVCz is considered to be very strong with regard to the hole transport.

The introduction of bulky and unsymmetric benzocarbazolyl chromophores instead of carbazolyl ones as a pendant group of vinyl polymers results in an increase in the exponential term related to the temperature in Eq. 1, because of the low T_0 values of P5VBCz and P7VBCz. However, the μ_0 values related to the molecular interaction ascribed to properties of the chromophores themselves are much lower for benzocarbazolyl polymers than for PVCz; consequently, the mobilities of both P5VBCz and P7VBCz are smaller than that of PVCz. Therefore, the introduction of benzocarbazolyl chromophores is not a good modification from the point of view of the carrier transport.

Carrier-photogeneration Efficiency. In order to excite the ^1L_b, ^1L_a, and ^1B_a absorption bands, narrow band-pass filters of 390, 330, and 270 nm were used for P5VBCz, and those of 370, 330, and 270 nm, for P7VBCz(Fig. 1). Figure 5 shows the field dependence of the carrier-photogeneration efficiency,ϕ, of P5VBCz and P7VBCz for the various excitation bands at 338 K, including that of PVCz for the sake of

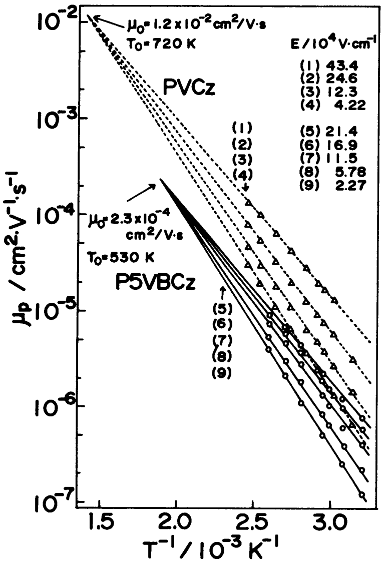

Fig. 3. Dependence of the hole drift mobility on temperature with electric field as a parameter.

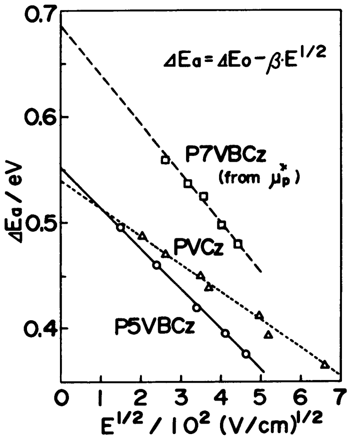

Fig. 4. Dependence of the activation energy ΔE_a on the electric field.

TABLE 1. TRANSPORT PARAMETERS[a)] AND GLASS TRANSITION TEMPERATURE, T_g

Sample[b)]	μ_0 / 10^{-3} cm^2/V·s	T_0 / K	E_0 / eV	β / 10^{-4} eV/$\sqrt{\text{V/cm}}$	T_g / K
P5VBCz	0.23	530	0.55	3.9	>544
PVCz[c)]	15	725	0.54	2.6	501
P5VBCz	* 0.14	530	0.54	3.4	>544
P7VBCz	* 0.21	490	0.69	4.7	544
PVCz[c)]	* 8.5	730	0.53	2.6	501
VCz-St copolymer[c)] (73 mol%)	* 9.0	720	0.57	2.6	—
VCz-St copolymer[c)] (50 mol%)	* 5.0	695	0.60	2.8	—

a) *: Values were determined from μ_p^*. b) The values in parentheses show the content of VCz. c) Ref. 21.

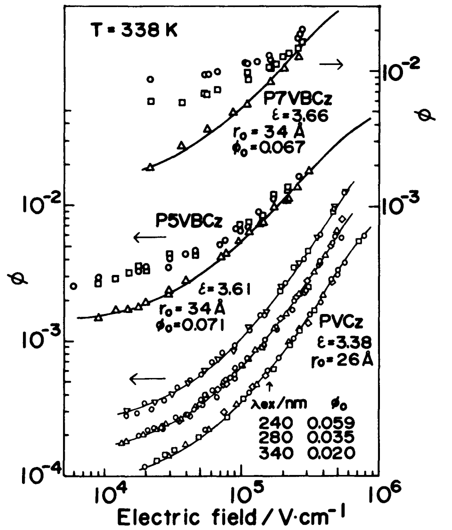

Fig. 5. Field dependence of the carrier-photogeneration efficiency in P5VBCz, P7VBCz, and PVCz films for different excitation bands. The solid lines were calculated from Eq. 1 in Ref. 20 with r_0 and ϕ_0 values presented in the figure. The keys ○, □, and △ present the ^1L_b, ^1L_a, and ^1B_a band excitation, respectively, except for PVCz.

comparison. The ϕ values of P5VBCz and P7VBCz were nearly equal to each other and were much larger than that of PVCz for all the excitation bands.

The solid lines in Fig. 5 were calculated from Eq. 1 in Ref. 20, with an interionic separation r_0 of 34 Å and with a primary yield of the electron-hole pair, ϕ_0, of 0.071 and 0.067 for P5VBCz and P7VBCz respectively; this equation is used in order to calculate the overall carrier-photogeneration efficiency, ϕ, given as the product of ϕ_0 and the dissociation probability, P(E), which is given by the Onsager theory of the geminate recombination of a bound electron-hole pair with r_0. The experimental data for the ^1B_a band were in good agreement with the lines predicted from the Onsager theory, indicating that the extrinsic carrier-photogeneration via an exciplex is predominant for the excitation of a surface layer of a film. However, the experimental data for the ^1L_b and ^1L_a bands did not fit the Onsager theory because of a contribution of another carrier-generation process, one independent of the electric field. On the other hand, the carrier-photogeneration efficiency of PVCz for all the excitation bands fit the Onsager theory, with both ϕ_0 values increasing from 0.02 to 0.059 and r_0 (=26 Å).²⁰⁾ The large r_0 value of both P5VBCz and P7VBCz is probably attributable to the fact that a large excess energy must be dissipated during the thermalization process from a non-relaxed exciplex state to the ion-pair state because the ionization potential of benzocarbazolyl chromophores is smaller than that of the carbazolyl chromophores.²⁸⁾

The results described above show that the introduction of benzocarbazolyl chromophores with a small ionization potential instead of carbazolyl ones is a good modification from the point of view of the carrier-photogeneration.

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