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Extrinsic Carrier-photogeneration in Poly(*N*-vinylcarbazole)

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The carrier-photogeneration efficiency of holes in poly(*N*-vinylcarbazole) (PVCz) films was investigated by means of the time-of-flight method as a function of applied electric field, temperature, and excitation band. The extrinsic effects on the efficiency were examined; these included photooxidation of film surface and doping with a weak electron-acceptor, dimethyl terephthalate (DMTP). The experimental results were analyzed according to the Onsager theory of geminate recombination of a bound electron-hole pair with an interionic separation of r_0. The primary yield of the electron-hole pair, ϕ_0, increased from 0.02 to 0.059 with decreasing excitation wavelength. By photooxidation, it increased up to 0.09 for all the excitation bands. The r_0 was independent of the excitation band, and was identical between fresh and photooxidized films. In DMTP(1.8 mol%)-doped films, both ϕ_0 and r_0 were independent of the excitation band, although their values were different from those of undoped films. These results indicate that the extrinsic carrier-photogeneration *via* nonrelaxed exciplexes formed between singlet excitons and acceptor-like impurities or photooxidation products is predominant in PVCz films for all the excitation bands.

A number of papers have appeared in the literature concerned with the carrier-photogeneration process in poly(*N*-vinylcarbazole) (PVCz), one of the typical photoconducting polymers.[1—10)] Taking account of the ionization potential (6.1 eV)[11)] and the electron affinity (1.5 eV)[12)] of PVCz in a solid film, the intrinsic carrier-photogeneration due to the autoionization mechanism, which has been observed for anthracene single crystals,[13)] is considered only for the π-π^* excitation higher than 4.6 eV (^1B_b and ^1B_a transitions). For the lower π-π^* excitation (^1L_b and ^1L_a transitions), the extrinsic carrier-photogeneration expressed by Scheme 1 is the most probable mechanism at the present stage.[10)] Photooxidation products of PVCz produced within the surface layer of a film seem to be the most probable as the acceptor-like impurity A in Scheme 1.[9)]

$$^1D^* + A \longrightarrow \underset{\substack{\text{encounter}\\ \text{complex}}}{(^1D^*\cdots A)} \longrightarrow \underset{\substack{\text{nonrelaxed}\\ \text{exciplex}}}{{}^1(D^+A^-)^{**}} \xrightarrow{\text{thermalization}}$$

$$\underset{\substack{\text{bound electron-hole}\\ \text{pair}}}{\overset{r_0}{{}^1(D^+\cdots A^-)}} \xrightarrow[P(E)]{\text{field-assisted dissociation}} \underset{\text{carriers}}{D^+ + A^-}$$

$$\Big\downarrow \substack{\text{geminate recombination}\\ 1\text{-}P(E)}$$

$$\underset{\text{relaxed exciplex}}{{}^1(D^+A^-)^*}$$

Scheme 1.

The overall carrier-photogeneration efficiency, ϕ, is given as the product of the primary quantum yield, ϕ_0, of a bound electron-hole pair with an interionic separation of r_0 and the dissociation probability, $P(E)$:

$$\phi = \phi_0\, P(E). \tag{1}$$

The ϕ_0 is considered to be independent of the electric field, E. The field-dependent probability of $P(E)$, which is given by the Onsager theory,[14)] is a function of r_0.

The field dependence of the photogeneration efficiency in PVCz films has been analyzed according to the Onsager theory by two groups of investigators.[4,8)] They have reported that ϕ_0 is independent of the excitation wavelength and that r_0 increases in steps with decreasing excitation wavelength. However, there has been no explanation of their results. These results are quite opposite to the predictions based on the extrinsic carrier-photogeneration process expressed by Scheme 1.

The above results were obtained by means of the xerographic discharge technique. Although it is convenient and practical, especially for high fields, this technique seems inferior to the time-of-flight method because it is difficult to avoid two effects: trapped space charge due to preexposures and photodegradation of film surface caused by exposing it to corona-charge. Unfortunately, to our knowledge, there have been few reports in which the field dependence of the photogeneration efficiency has been measured in detail by means of the time-of-flight method, taking cautions to prevent any photooxidation of the films, and has been analyzed according to the Onsager theory.

In the present paper, in order to make clearer the carrier-photogeneration process, we investigate effects of the excitation wavelength and temperature on the photogeneration efficiency in PVCz over a wide range of fields by means of time-of-flight method. We also investigated the photogeneration efficiency in PVCz films which were slightly-photooxidized or doped with dimethyl terephthalate (DMTP), a weak electron acceptor, by comparing the results with that obtained for the fresh films.

Experimentals

The PVCz was prepared by free-radical polymerization (initiator: AIBN) of the highly-purified monomer and was purified by reprecipitation from a benzene solution with methanol several times. The polymer sample was stored in tubes with an argon atmosphere in the dark. Gel permeation chromatography analysis showed $M_n = 1.95\times10^5$ and $M_w/M_n = 2.3$. Films were cast on NESA-coated quartz plates from a benzene solution and were dried *in vacuo*. Photooxidized films were prepared by irradiating the free surface of fresh films in air for 1—18 min through a water filter (10 cm) with the full spectrum of a 500 W high pressure mercury lamp at a distance of 40 cm from the lamp. A semitransparent gold electrode with a typical area of 1 cm² was evaporated on a film to prepare a sandwich-type cell. Caution was taken in all procedures of the experiment to keep the sample from being exposed to the room light. Film thickness was determined from the weight and density (1.188 g/cm^3) of a film with a known area (*ca.* 1.5 cm^2) and/or by a capacitive method.

A 3 µs light pulse from an air-gap flash was irradiated on a cell set in a cryostat with a high vacuum, better than 1.3 mPa, through appropriate narrow band pass filters. An induced transient photocurrent was observed through a series load resistor in the current or differential mode by means of a storage oscilloscope. In order to avoid the space charge effect due to previous exposures and to get reproducible results, the cell was irradiated by visible light (λ>450 nm) while short-circuited for several minutes prior to each measurement. The intensity of each light pulse was monitored by a Si photodiode equipped with a peak-hold circuit, the output of which was calibrated by means of a potassium ferrioxalate actinometer.

The dielectric constant ε of films was determined from capacitance measurements. The value of 3.38, which was determined at the frequency of 1 kHz at 23 °C, was used in the calculation of $P(E)$, neglecting the temperature dependence of ε.

The $P(E)$ was calculated according to the method developed by Geacintov and Pope.[15]

Results and Discussion

Effects of Excitation Band and Temperature on ϕ_0 and r_0 in Fresh Films. As shown in Fig. 1, three kinds of band bass filters were used in order to excite the ^1L_b, ^1L_a, and ^1B_a absorption bands. 90% of the incident light of 340, 280, and 240 nm was absorbed within layers of less than 0.51, 0.23, and 0.065 µm in depth, respectively. A typical set of transient photocurrent signals for positive gold-electrode illumination is shown in Fig. 2. The observed photocurrent signal generally had an initial spike-like signal superimposed on a longer-duration signal. This spike-like signal cannot be attributed to loss of holes by bimolecular volume-recombination in the excitation layer, as for the case of anthracene,[17] but to fast hole transport in a short duration immediately after carrier generation.[18] The number of collected carriers (holes) per unit area, N_p, was obtained from the integral of the photocurrent over the entire drift times using a set of transient signals such as shown in Fig. 2. The N_p was proportional to the light intensity, ranging from 1×10^{12} to 1×10^{14} photons/cm^2 pulse, and was independent of the film thickness, which ranged from 3 to 12 µm. These results indicate that the observed values of N_p are not affected by space-charge effects, bulk recombination, or range limitation of hole carriers. The ϕ was obtained by dividing N_p by the light intensity.

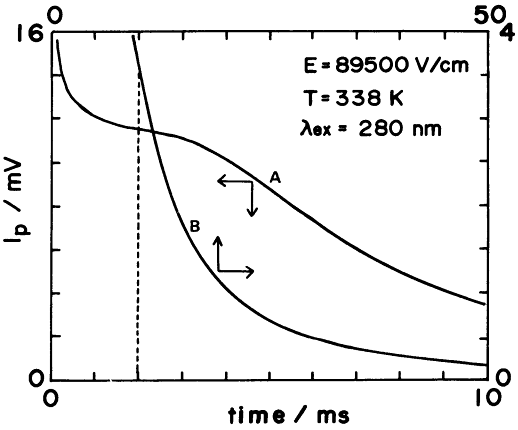

Fig. 2. A set of typical transient photocurrent signals.
(A) The early part of a signal, (B) the late part of a signal.

Figure 3 shows the field dependence of ϕ in fresh films for the different excitation bands. The measurements were done at 65 °C in order to avoid the complicating effects due to bulk carrier trapping in the low-field region.[2] The ϕ increased in the order of the

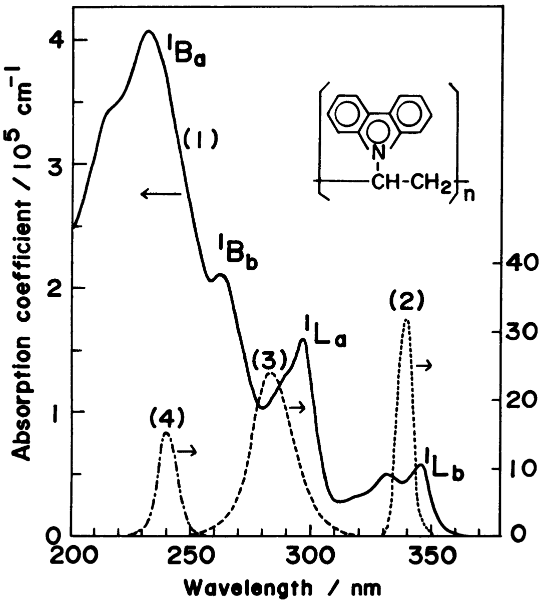

Fig. 1. Absorption spectrum of a PVCz film (1) and transmittance of band pass filters ((2)—(4)).

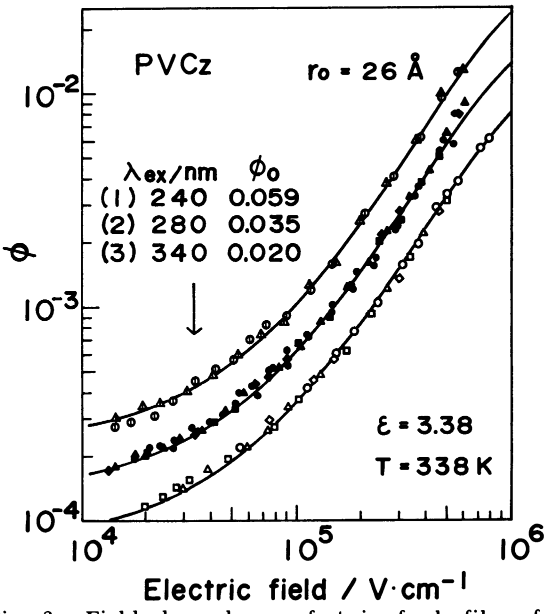

Fig. 3. Field dependence of ϕ in fresh films for different excitation bands. The solid lines were calculated from Eq. 1 with r_0 and ϕ_0 values presented in the figure.

^1L_b, ^1L_a, and ^1B_a bands. The solid lines were calculated from Eq. 1, with r_0 of 26 Å and with ϕ_0 of 0.020, 0.035, and 0.059 for the ^1L_b, ^1L_a, and ^1B_a bands, respectively. They are in good agreement with the experimental data. The results indicate that the increase in ϕ with decreasing excitation wavelength is due only to a change in ϕ_0. Although being quite opposite to the results reported in the literature,[4,8] these results are explained by the extrinsic carrier-photogeneration process (Scheme 1) mentioned below.

The singlet excitons, which migrate in a film to encounter molecules A, are the lowest excited singlet state, irrespective of the excitation wavelength, because the internal conversion from any higher excited singlet state to the lowest excited one precedes excitation energy migration. Therefore, r_0 is independent of the excitation wavelength. Taking account of the singlet exciton migration efficiency,[16] ϕ_0 is considered to increase with increasing concentration of A in the concentration range less than the order of 10^{-3} mol/mol-basic-unit (expressed by mol% hereafter). As the photooxidation proceeds preferentially near the surface of a film, the concentration of photooxidation products acting as A in Scheme 1 becomes higher on going from the bulk to the surface. Because of this concentration profile, ϕ_0 has a tendency to be higher for the excitation wavelength having higher absorption coefficient; that is, ϕ_0 increases in the order of the ^1L_b, ^1L_a, ^1B_b, and ^1B_a transitions.

Figure 4 shows the temperature dependence of ϕ in fresh films for the 340 nm excitation. The solid lines were calculated from Eq. 1 with r_0=26 Å and ϕ_0=0.020, assuming that both r_0 and ϕ_0 were independent of temperature. They are in fairly good agreement with the experimental data, indicating that both r_0 and ϕ_0 do not depend on temperature in the relatively narrow range. The result for ϕ_0 seems to be due to the fact that the singlet exciton migration length is insensitive to temperature in this range.[16]

Effects of DMTP-doping on ϕ_0 and r_0. Figure 5 shows the field dependence of ϕ in films doped with DMTP (1.8 mol%). The ϕ in these films is much larger than that in undoped films and is independent of the excitation bands. The data are in fairly good agreement with the solid line calculated from Eq. 1 with r_0= 22 Å and ϕ_0=0.9. In the DMTP-doped films, the host excimer fluorescence was almost completely replaced by the exciplex fluorescence,[16] indicating that most of the singlet excitons encounter DMTP molecules to form encounter complexes. Furthermore, the probability of triplet exciton formation from a singlet exciton by intersystem crossing is in the order of 10^{-2}.[19] It is, therefore, reasonable that the DMTP-doped films

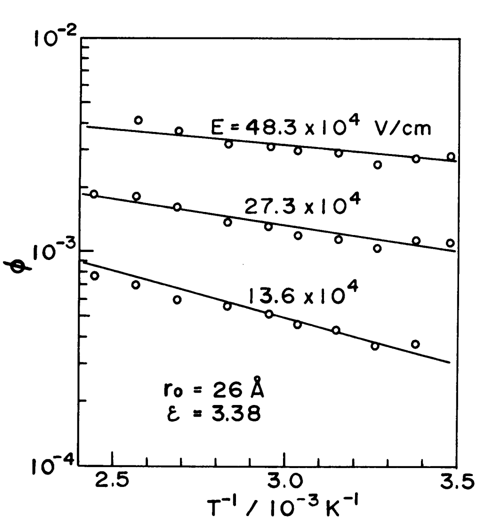

Fig. 4. Temperature dependence of ϕ in fresh films for the 340 nm excitation. The solid lines were calculated from Eq. 1 with r_0=26 Å and ϕ_0=0.020.

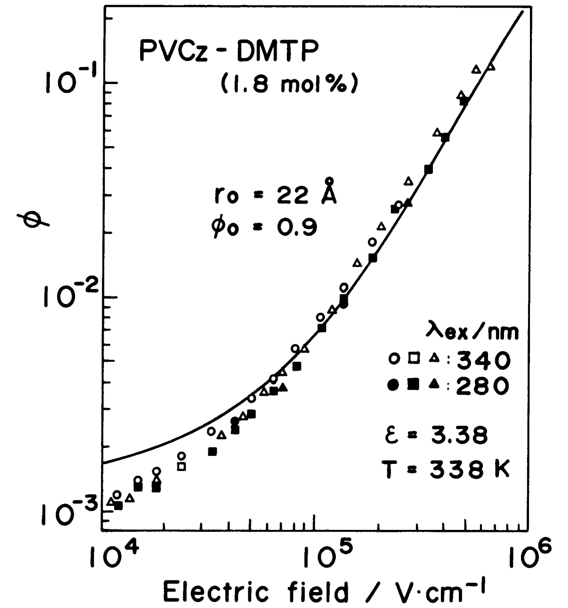

Fig. 5. Field dependence of ϕ in films doped with DMTP (1.8 mol%). The solid line was calculated from Eq. 1 with r_0=22 Å and ϕ_0=0.9.

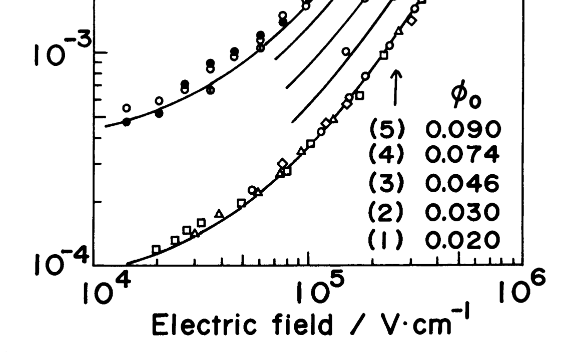

Fig. 6. Field dependence of ϕ in photooxidized films for different irradiation times. The solid lines were calculated from Eq. 1 with r_0 and ϕ_0 values presented in the figure. The irradiation time: (1) 0, (2) 0.9, (3) 3.3, (4) 9, and (5) 18 min. See the text concerning the irradiation conditions.

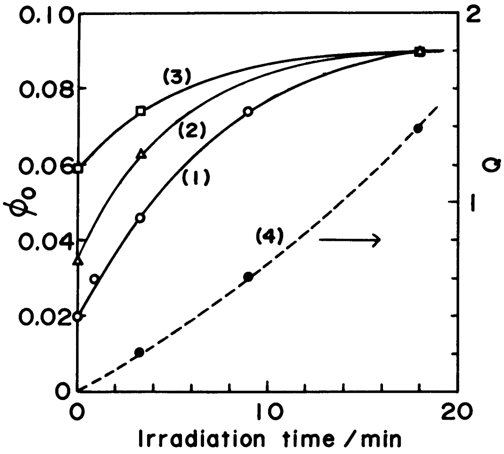

Fig. 7. Irradiation-time dependence of ϕ_0 and the quenching factor, Q, of the excimer fluorescence. ϕ_0: (1) 340 nm, (2) 280 nm, and (3) 240 nm excitation. Q: (4) 340 nm excitation.

have the ϕ_0 value of 0.9 for all the excitation bands. This high value of ϕ_0 is comparable to the value of 0.8 for PVCz films doped with 1,2,4,5-tetracyanobenzene (2 mol%) on excitation of the charge transfer band,[20] and is much larger than the value of 0.23 for films doped with 2,4,7-trinitro-9-fluorenone (6 mol%).[21] The r_0 value of 22 Å is the same as that observed from the quenching experiment of the exciplex fluorescence by electric field.[10]

Effects of Photooxidation on ϕ_0 *and* r_0. Figure 6 shows the field dependence of ϕ in photooxidized films for different irradiation times. The data are in good agreement with the solid lines calculated from Eq. 1 with r_0=26 Å, the same value as in fresh films, irrespective of both the excitation bands and the irradiation time. The ϕ_0 values thus determined are shown in Fig.7 as a function of irradiation time. The ϕ_0 increased rapidly with increasing irradiation time and soon leveled off to a value of 0.09 for all the excitation bands. The increase in ϕ with increasing irradiation time within the present level of photooxidation is thus explained by the increase in ϕ_0 only, which was caused by an increase in the concentration of acceptor-like photooxidation products acting as molecule A in Scheme 1.

The films irradiated in air showed remarkable changes in the fluorescence spectra, while such changes were not observed for the films irradiated in a high vacuum of 1.3×10^{-3} Pa. With irradiation time, the excimer fluorescence of PVCz films decreased and a new fluorescence band, which has been attributed to the exciplex formed between an excited carbazole chromophore and an acceptor-like photooxidation product,[9] appeared around 515 nm. The decrease in the excimer fluorescence in films is shown in Fig. 7, using a quenching factor *Q*. In each film, the value of *Q* for the 280 nm excitation was roughly twice as large as that for the 340 nm excitation. According to the random hopping model of singlet exciton migration, *Q* is expressed by Eq. 2:

$$Q=([\mathrm{A}])+[\mathrm{T_s}])/[\mathrm{E}], \qquad (2)$$

where [A] is the concentration of acceptor-like photooxidation products acting as molecule A in Scheme 1; [$\mathrm{T_s}$] is the concentration of non-acceptor-like photooxidation products acting as singlet exciton traps; and [E] is the concentration of the excimer-forming sites. According to Scheme 1, ϕ_0 is expressed by Eq. 3:

$$\phi_0=\phi_s{}^*[\mathrm{A}]/([\mathrm{E}]+[\mathrm{A}]+[\mathrm{T_s}]), \qquad (3)$$

where $\phi_s{}^*$ is the quantum yield of the singlet exciton formation. The [$\mathrm{T_s}$] and [A] were evaluated from the *Q* and ϕ_0 values, taking [E] and $\phi_s{}^*$ as 0.27 mol%[16] and 0.9,[19] respectively, irrespective of the irradiation time. The [$\mathrm{T_s}$] and [A] thus obtained are listed in Table 1. They are the effective concentrations in the surface layer through *ca.* 0.5, 0.2, and 0.07 μm in depth for the 340, 280, and 240 nm excitations, respectively. Both [$\mathrm{T_s}$] and [A] were higher for the shorter-wavelength excitation, because the photooxidation proceeds preferentially near the surface of a film. With increasing irradiation time, both [A] and [$\mathrm{T_s}$] increased, but their ratio, [A]/[$\mathrm{T_s}$], decreased. This is reasonable, judging from the facts that the acceptor-like photooxidation products are intermediates and undergo further photooxidation and that the exciplex fluorescence around 515 nm was observed most strongly for the films with the *Q* value of 1—3.[9] The small value (0.09) of ϕ_0 observed for all the excitation bands is thus explained by a small value of the ratio, [A]/([E]+[A]+[$\mathrm{T_s}$]), and is independent of the excitation layer.

The ϕ_0 values of 0.11[8] and 0.14[4] determined by the xerographic discharge technique are comparable to the value of 0.09 in the photooxidized films and are much larger than the value of 0.02 for the 340 nm excitation in fresh films. This suggests that the surface of films exposed to xerographic photo-discharge even in a nitrogen atmosphere is subjected to the photooxidation at a fairly high level.

The r_0 is considered to depend on the properties of acceptor-like molecules,[10] while both the fresh and photooxidized films had the identical value (26 Å) of r_0. This suggests that the main acceptor-like molecules are identical for these films. The r_0 is considered to depend on the excess energy to be dissipated. It was,

TABLE 1. EFFECT OF IRRADIATION TIME ON [A] AND [$\mathrm{T_s}$][a]

Irradiation time	[A]/mol%			[$\mathrm{T_s}$]/mol%	
min	340 nm	280 nm	240 nm	340 nm	280 nm
0	0.006	0.011	0.018	≈0	≈0
3.3	0.016	0.028	—	0.019	0.077
9	0.036	—	—	0.124	—
18	0.065	0.10	—	0.315	0.67

a) 340, 280, and 240 nm are the excitation wavelengths. See the text.

nevertheless, independent of the excitation bands, as mentioned above. This indicates that the direct carrier-photogeneration from the higher excited singlet states is negligible for films investigated in this paper.

Based on the energetical considerations,[10,11] intrinsic carrier-photogeneration due to the autoionization mechanism is expected to be possible for the ^1B_b and ^1B_a excitations. Yokoyama *et al.* have proposed this mechanism for the photocurrent in copolymers of *N*-vinylcarbazole with 1-vinylnaphthalene.[22] However, the comparison of r_0 and ϕ_0 between the 240 nm excitation and the 280 or 340 nm excitation clearly indicates that the extrinsic carrier-photogeneration in Scheme 1 rather than the intrinsic autoionization mechanism is predominant even for the 240 nm excitation. This is reasonable, judging from both the relatively high concentration of acceptor-like impurities ([A]=0.018 mol%) in the surface layer through 0.07μm in depth of fresh PVCz films and the relatively low value of the primary quantum yield ($\phi_0<10^{-2}$) for the autoionization process in anthracene single crystals.[23] The intrinsic autoionization mechanism is considered to become important when the higher singlet excited states are formed in a bulk sample which has a low concentration of acceptor-like impurities, as is the case of the triplet-triplet annihilation in the copolymers.[22]

Conclusion. As mentioned above, the excitation wavelength dependences of r_0 and ϕ_0 in fresh, photooxidized and DMTP-doped films lead to the conclusion that the extrinsic carrier-photogeneration process expressed by Scheme 1 and Eq. 1 is predominant in every film for all the excitation bands.

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