The Photoconductivity of Poly(*N*-vinylcarbazole). V.[1] The Doping Effects of Various Materials on the Photoconductivity[2]

Kenichi Okamoto,* Shigekazu Kusabayashi,* and Hiroshi Mikawa

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

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The photoconductivity and fluorescence spectra of poly(*N*-vinylcarbazole) (PVCz) films doped with various materials were investigated. The photoconductive properties of doped films may be grouped into three classes according to the kind of dopant. The doping of an electron donor, such as tetramethyl-*p*-phenylenediamine and 1,5-diaminonaphthalene, reduced the photocurrent in all the wavelength regions by a factor of 10^2 to 10^4 because of the hole-trapping effect of the dopant molecule. The exciplex formed between the donor and PVCz does not seem to contribute to the photocurrent. The doping of an acceptor, such as TCNE and dimethyl terephthalate, on the other hand, enhanced the photocurrent. The field-assisted thermal dissociation of an excited CT complex formed between PVCz and an acceptor seems to be a carrier generation process. The doping of anthracene or perylene quenched the fluorescence of PVCz by a factor of 10 to 30 and reduced the photocurrent in the UV region by a factor of 2 to 7, while it enhanced the photocurrent in the absorption region of the dopant.

In their previous papers[1,3] the present authors have examined the photoconductivity of PVCz and explained it by assuming that the carriers were generated through the field-assisted thermal dissociation of an exciplex formed with a fairly good efficiency between PVCz and some impurity with an electron-accepting ability, and also through the detrapping of trapped carriers by singlet excitons, and that the carriers migrated through the overlap of the π-electrons of the neighboring carbazyl rings in the same polymer chain.

In the present paper the doping effects of various materials on the photoconductivity and the fluorescence spectra of PVCz were examined.

Experimental

Materials. *PVCz*: The preparation of PVCz was described in a previous paper.[3]

Carbazole: A commercial product was subjected to a Diels-Alder reaction with maleic anhydride in order to remove a trace of anthracene[4], and was then purified by repeated recrystallizations from *o*-dichlorobenzene and subsequently from acetone.

Anthracene: A commercial product of a scintillation grade was recrystallized three times from benzene.

Perylene, Tetracyanoethylene (TCNE) and Dimethyl terephthalate (DMTP): Commercial products were recrystallized two or three times from benzene and subsequently sublimed *in vacuo*.

*Tetramethyl-*p*-phenylenediamine (TMPD) and 1,5-Diaminonaphthalene (DAN)*: A commercial product of the HCl salt was reprecipitated twice from an aqueous solution of ammonia and then recrystallized three times from *n*-hexane or benzene under a nitrogen stream.

p-*Nitroaniline (PNA)*: A commercial product was recrystallized three times from methanol. The solvents were purified by the ordinary method.

Measurements. Doped films were prepared by casting a 5 wt% benzene solution of PVCz with a certain amount of a dopant onto a quartz plate in a manner similar to that described previously.[3] The films of the following doping amounts were used in the measurements: carbazole 2.0 mol% (per carbazole unit in PVCz), anthracene 3.0 mol%, perylene 1.4 mol%, TMPD 1.8 mol%, DAN 2.7 mol%, TCNE 1.8 mol%, DMTP 1.8 mol%, and PNA 1.9 mol%. The thickness of the films was about 15 μ for the electrical measurements and about 1—2 μ for the fluorescence measurements. The preparation of a sandwich-type cell of a film (area of electrode, 1 cm^2) and the electrical measurement were carried out in a manner similar to that described previously.[3] The ESR spectrum of PVCz powder doped with TCNE (8 mol%) was also measured under illumination with UV or visible light from a 500 W superhigh pressure Hg lamp as well as in the dark.

Results

Dark Conductivity. Carbazole, anthracene, perylene, DMTP, TMPD, and PNA did not have any significant effect on the conductive properties (the magnitude of the dark current, the voltage dependence, and the activation energy) of a PVCz film in the dark.[5]

On the other hand, the doping of DAN or TCNE changed the conductive properties. The dark current for a film doped with DAN was much smaller than that of an undoped film by a factor of ten to a hundred. It was ohmic over the applied fields (0—100000 V/cm). Its activation energy (ΔE_d in the $i_d \propto \exp(-\Delta E_d/kT)$ equation) was 0.9 eV below 100 °C and 1.5 eV above 100 °C, as is shown in Table 1. The former value is similar to that of an undoped film, while the latter is considerably larger. The doping of TCNE enhanced the dark current by a factor of several hundreds to a thousand and lowered the value of ΔE_d (0.8 eV) a little.

Shape of the Photoresponse. The doping of carbazole, anthracene, perylene, or PNA did not have any effect on the photoresponse behavior. The films doped with these materials showed photoresponse curves

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* Present address: Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi.

[1] Part IV of this series, K. Okamoto, K. Kato, K. Murao, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 2883 (1973).

[2] A part of the experimental results in this paper was presented at the 26th Symposium of the Society of Electrophotography of Japan, Osaka, November, 1970.

[3] K. Okamoto, S. Kusabayashi, and H. Mikawa, Part III of this series, This Bulletin, **46**, 2324 (1973).

[4] K. Kihara, T. Ishii, Y. Suzuki, and T. Takeuchi, *Kogyo Kagaku Zasshi*, **73**, 2632 (1970).

[5] K. Okamoto, S. Kusabayashi, and H. Mikawa, Part II of this series, This Bulletin, **46**, 1953 (1973).

TABLE 1. ACTIVATION ENERGIES OF PHOTO AND DARK CONDUCTIVITIES

Doping material	$\Delta E_{\rm d}$ (eV)	$\Delta E_{\rm ph}$ (eV)	Wavelength of illuminating light (mμ)
Carbazole	1.1	0.17	350
Anthracene	1.1	0.14	360
		0.13	380
Perylene	1.0	0.12	350
		0.15	440
TMPD	0.93—1.2	0.24 (below 80 °C)	360
		0.50 (80—140°C)	360
DAN	0.9 (below 100 °C)	0.25 (below 100 °C)	350
	1.3—1.6 (100—140 °C)	0.44 (100—140 °C)	350
TCNE	0.82	0.22	350
		0.24	550
DMTP	1.0—1.1	0.19 (below 90 °C)	350
		0.33 (90—160°C)	350
PNA	—	0.23	360
		0.25	430
Undoped	1.0—1.3	0.13—0.22	UV
		0.07—0.16	Visible

similar to those observed in an undoped film.

The doping of DMTP did not have any effect in the photoresponse behavior when a negative electrode was illuminated (this photocurrent is abbreviated to $i_{\rm ph}^-$) or when a positive electrode was illuminated by the light of longer wavelength than 360 mμ, but it caused a considerable space charge effect on the photocurrent when a positive electrode was illuminated by UV light (this photocurrent is abbreviated to $i_{\rm ph}^+$). $i_{\rm ph}^+$ in the region shorter than 360 mμ reached a peak value soon after light-on and decreased slowly with time until it leveled off to a steady-state value after 10—40 min. The steady-state value was much smaller than the peak value, especially when the light of the wavelength corresponding to the absorption peak was used. This difference between the peak and the steady values was quite large as compared with the case of an undoped film.

In a film doped with TCNE or DAN, the normal photoresponse curve (A type in the previous paper³⁾) was observed at every wavelength irrespective of the polarity of the illuminated electrode.

Light-intensity Dependence of the Photocurrent. In every doped film except TCNE, the photocurrent was found to be proportional to the light intensity, irrespective of both the polarity of an illuminated electrode and the wavelength of light. This is the same as the case of a PVCz film. In a film doped with TCNE, the photocurrent was found to be proportional to the 0.8-th power of the light intensity.

Voltage Dependence of the Photocurrent. In films with dopants other than TMPD and DAN, the photocurrent showed a voltage dependence similar to that observed in an undoped film, as is shown in Fig. 1.

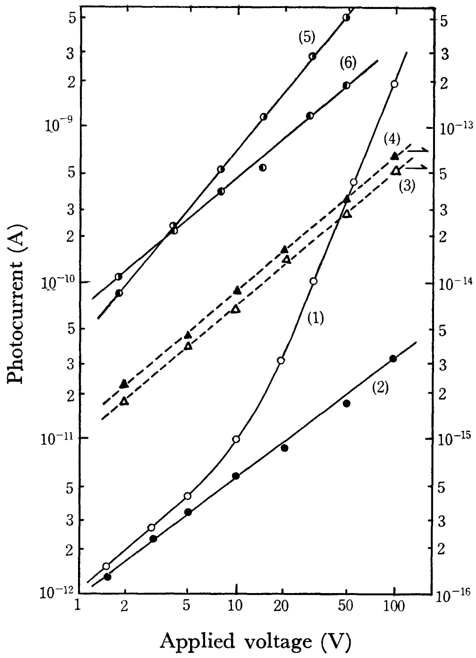

Fig. 1. Voltage dependence of photocurrent in doped films at 20 °C in high vacuum.
(1) perylene, $i_{\rm ph}^+$, 350 mμ; (2) perylene, $i_{\rm ph}^-$, 350 mμ; (3)DAN, $i_{\rm ph}^+$, 360 mμ; (4) DAN, $i_{\rm ph}^-$, 360 mμ; (5) TCNE, $i_{\rm ph}^+$, 350 mμ, and (6) TCNE, $i_{\rm ph}^+$, 550 mμ.

In applied fields higher than 15000 V/cm, $i_{\rm ph}^+$ was proportional to the n-th power of the applied voltage (n=1.4—2.0) in the UV region shorter than 360 mμ, although it was proportional to the applied voltage in the visible region. The $i_{\rm ph}^+$ in applied fields lower than 15000 V/cm and the $i_{\rm ph}^-$ were proportional to the applied voltage, irrespective of the wavelength of light. In these films $i_{\rm ph}^+$ was larger than $i_{\rm ph}^-$ in high fields, although they were roughly equal to each other in low applied fields. This behavior is similar to the case of an undoped film.

On the other hand, in a film doped with TMPD or DAN both $i_{\rm ph}^+$ and $i_{\rm ph}^-$ were proportional to the applied voltage over the whole voltage region, and the superlinear dependence of $i_{\rm ph}^+$ in the high-field region was not observed. There was no significant difference in magnitude between $i_{\rm ph}^+$ and $i_{\rm ph}^-$ in these films, as is shown in Fig. 2(b). It should be noted that these dopants are fairly strong electron donors.

Spectral Dependence of the Photocurrent. The spectral dependence of the photocurrent in the doped films shown in Figs. 2(a—d) was obtained by normalizing the observed photocurrent values to the values for the light intensity of 2×10^{13} photons/cm²s according to the light-intensity dependence. The photocurrent values in Fig. 2 were obtained from the cells which showed the representative values of photocurrent among several cells. The magnitudes of the photocurrents in Figs. 2 can be compared directly with each other. The dopants are grouped according to both their spectral dependence and the magnitudes of the photocurrents. Figures 2(a—d) also show the absorption spectra of the undoped and doped films used in the photoconductivity measurements. No new absorption

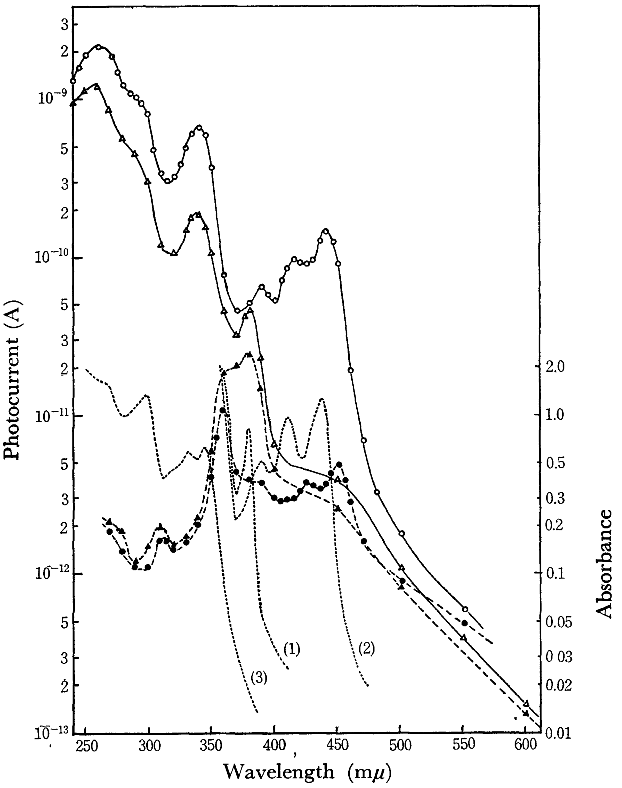

Fig. 2(a). Spectral dependence of photocurrent in a sandwich-type cell of a PVCz film doped with anthracene or perylene under 35000 V/cm in high vacuum at 20° C.
Film doped with anthracene; —△— for i_{ph}^+, and ---▲--- for i_{ph}^-.
Film doped with perylene; —○— for i_{ph}^+, and ---●--- for i_{ph}^-.
The absorption spectra of the PVCz films are given by the dotted lines. (1) doped with anthracene, (2) doped with perylene, and (3) an undoped film 1 μ thick (This spectrum is given in order to show the π—π* bands of PVCz).

band was observed in the doped films except in the case of TCNE. The film doped with TCNE shows the charge-transfer (CT) absorption bands, as is well known.[6]

Group A. Carbazole, anthracene, and perylene belong to this group. The spectral dependence of the photocurrent is almost the same as that observed in an undoped film, as is shown in Figs. 2(a) and (c). The spectral dependence of i_{ph}^+ corresponds to the absorption spectrum, while that of i_{ph}^- corresponds inversely to it. In the film doped with anthracene or perylene, new photocurrent peaks are observed in the absorption region of the dopant. This sensitized photocurrent in the film doped with perylene showed a spectral dependence similar to that in the π-π* absorption bands of PVCz. The doping of carbazole hardly changed the magnitude of the photocurrent at all in any of the wavelength regions. The doping of anthracene or perylene reduced the photocurrent in the absorption region of PVCz by a factor of 2 to 7, while it enhanced the photocurrent in the lowest absorption band of the dopant by factors of 10 for i_{ph}^+ and 2—3 for i_{ph}^-.

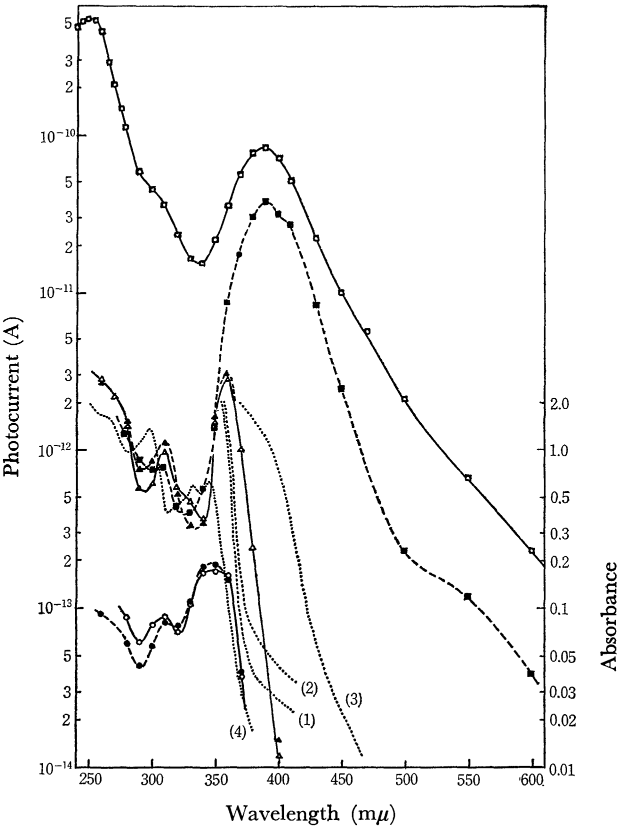

Fig. 2(b). Spectral dependence of photocurrent in a sandwich-type cell of a PVCz film doped with TMPD, DAN, or PNA under 35000 V/cm in high vacuum at 20 °C.
Film doped with TMPD; —△— for i_{ph}^+, and ---▲--- for i_{ph}^-.
Film doped with DAN; —○— for i_{ph}^+, and ---●--- for i_{ph}^-.
Film doped with PNA; —□— for i_{ph}^+, and ---■--- for i_{ph}^-.
The absorption spectra of the PVCz films are given by the dotted lines. (1) doped with TMPD, (2) doped with DAN, (3) doped with PNA, and (4) an undoped film 1 μ thick.

Group B. TMPD, DAN, and PNA belong to this group. As is shown in Fig. 2(b), both i_{ph}^+ and i_{ph}^- showed the same spectral dependence, one which corresponded rather inversely to the absorption spectrum, and both were significantly reduced in magnitude by doping.

In a film doped with TMPD or DAN, both i_{ph}^+ and i_{ph}^- significantly decreased in all the wavelengthr egions. The decrease in the photocurrent was 1/1000—1/10000 for i_{ph}^+ or 1/30—1/300 for i_{ph}^- in the case of DAN, while it was 1/100—1/10000 or 1/5—1/20 in the case of TMPD, respectively. Thus, i_{ph}^+ decreased much more than i_{ph}^-; hence, i_{ph}^+ was almost equal to i_{ph}^- in magnitude in all the wavelength regions. It is very interesting that the photocurrent decreased by a factor of 10^2—10^4 by the doping of small amount (1—3 mol%) of TMPD or DAN.

In a film doped with PNA, the photocurrent in the absorption region of PVCz decreased by a factor of 10—100 for i_{ph}^+ and by one of 5—10 for i_{ph}^-. The value of i_{ph}^+ was, however, still larger than i_{ph}^-, although the $i_{\mathrm{ph}}^+/i_{\mathrm{ph}}^-$ ratio in the UV region (4—30 in this case) was considerably smaller than the corresponding ratio of an undoped film (50—500). In a film doped with

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[6] H. Meier, W. Albrecht, and U. Tschirwitz, *Ber. Bunsenges. Physik. Chem.*, **73**, 795 (1969).

[7] J. Tanaka, This Bulletin, **36**, 833 (1963).

PNA, the incident light of wavelength shorter than 385 mμ was absorbed almost completely. Consequently, a photocurrent peak was not observed at 360 mμ, but at 390 mμ. In the wavelength region from 380 mμ to about 500 mμ, the photocurrent was a little larger than that of an undoped film.

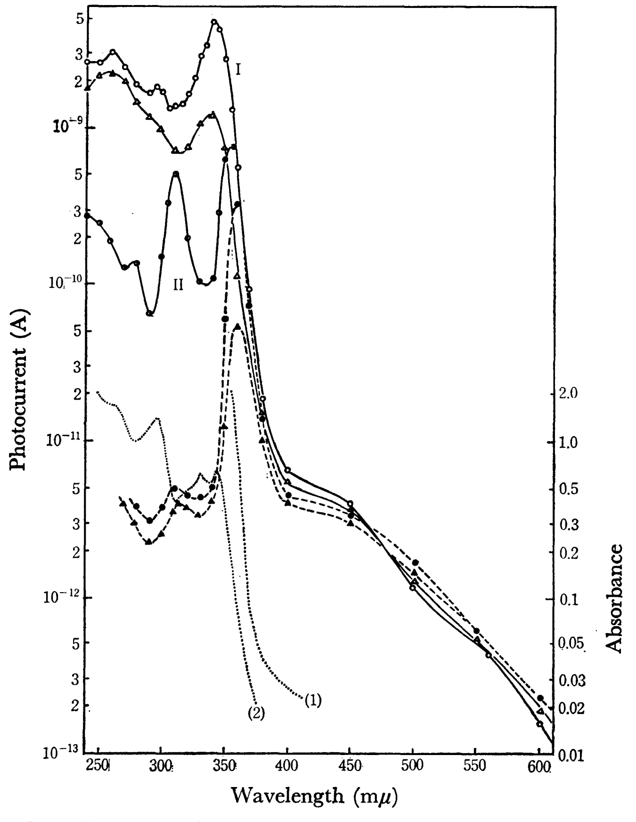

Fig. 2(c). Spectral dependence of photocurrent in a sandwich-type cell of both a PVCz film and a PVCz film doped with DMTP under 35000 V/cm in high vacuum at 20 °C.
PVCz; —△— for i^+_{ph}, and ---▲--- for i^-_{ph}.
Film doped with DMTP; the curves I and II for i^+_{ph} (see the text) and ---●---for i^-_{ph}.
The absorption spectra of the PVCz films are given by the dotted lines. (1) doped with DMTP and (2) an undoped film 1 μ thick.

Group C. DMTP belongs to this group. In a film doped with DMTP the spectral dependence of i^-_{ph} was almost the same as that observed in an undoped film. The spectral dependence of i^+_{ph}, however, changed with the measurement conditions, as is shown in Fig. 2(c), because of a considerable space charge effect. In Fig. 2(c) Curve I shows the spectral dependence of i^+_{ph} measured under conditions which make the space-charge effect as small as possible. In order to release space charges formed by the previous UV illumination, the visible light of wavelengths longer than 400 mμ was used for a long time in each case before UV light was used for the measurement. Curve II shows the spectral dependence of i^+_{ph} measured after space charges were built up by the preillumination of the UV light of wavelengths shorter than 330 mμ. In Curve I the spectral dependence was similar to that of an undoped film, and the magnitude of i^+_{ph} in the UV region was considerably larger than the magnitude of i^+_{ph} in an undoped film; that is, the chemical sensitization of the photocurrent was observed. On the other hand, in Curve II the spectral dependence corresponded inversely to the absorption spectrum, and the magnitude of i^+_{ph} in the UV region, especially at the absorption peaks, was considerably smaller than that of an undoped film.

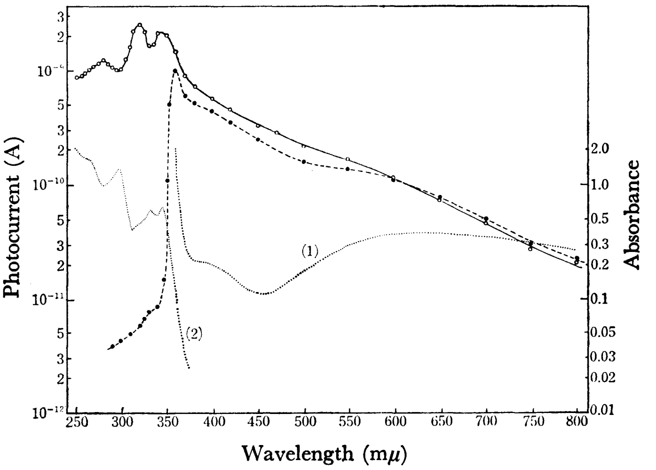

Fig. 2(d). Spectral dependence of photocurrent in a sandwich-type cell of a PVCz film doped with TCNE under 35000 V/cm in high vacuum at 20 °C.
—○— for i^+_{ph}, and ---●--- for i^-_{ph}.
The absorption spectra of the PVCz films are given by the dotted lines. (1) doped with TCNE and (2) an undoped film 1 μ thick.

Group D. TCNE belongs to this group. The peaks of i^+_{ph} were observed at 340 and 320 mμ, and the minima, at 330 and 295 mμ, as is shown in Fig. 2(d). The i^-_{ph} showed only a peak at 360 mμ and showed neither a clear peak nor a minimum in the wavelength region shorter than 350 mμ. The doping of TCNE enhanced both i^+_{ph} and i^-_{ph} a little in the UV region and significantly in the visible region. The degree of increase in the photocurrent in the UV region was 10—20 fold at 360 mμ, 3—4 fold at 350 mμ, and 2 fold at 330 mμ. Thus, the doping of TCNE caused not only the spectral sensitization, but also the chemical sensitization of the photocurrent.

Activation Energy of Photocurrent. The activation energies of the photocurrent (ΔE_{ph}) in doped films are listed in Table 1. In a film doped with carbazole, anthracene, or perylene, the value of ΔE_{ph} (0.15—0.20 eV) was almost the same as that observed in an undoped film. In a film doped with PNA, or TCNE, the value of ΔE_{ph} was 0.2—0.3 eV, a little larger than that of an undoped film. In a film doped with TMPD, DAN, or DMTP, the photocurrent showed clearly different temperature dependences in the high- and low-temperature ranges, as is shown in Fig. 3. In these films, ΔE_{ph} was 0.19—0.25 eV in the low-temperature range and 0.35—0.50 eV in the high-temperature range, the latter being fairly large. Although the values of ΔE_{ph} mentioned above were the values for the photocurrent in the absorption region of PVCz, similar values of ΔE_{ph} were also obtained for the spectrally-sensitized photocurrent.

Fluorescence Spectra of the Doped Films. Information

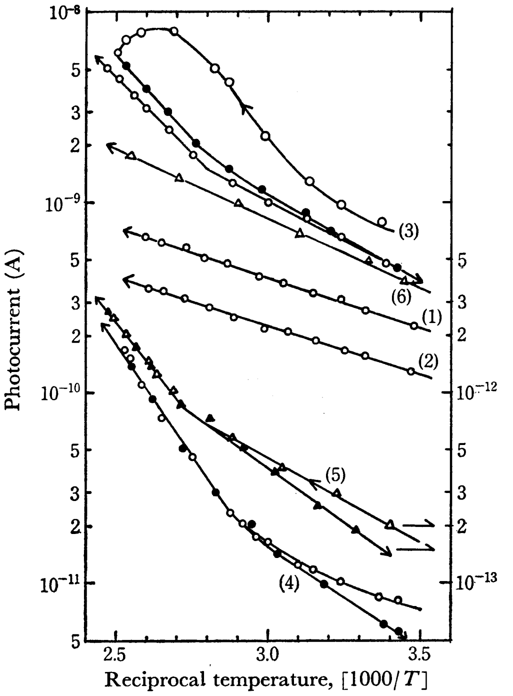

Fig. 3. Temperature dependence of photocurrent in a sandwich-type cell of the doped PVCz films under 35000 V/cm with positive electrode illumination in high vacuum. (1) perylene, 350 mμ, (2) perylene, 440 mμ, (3) DMTP, 360 mμ, (4) TMPD, 360 mμ, (5) DAN, 350 mμ, and (6) undoped, 350 mμ.

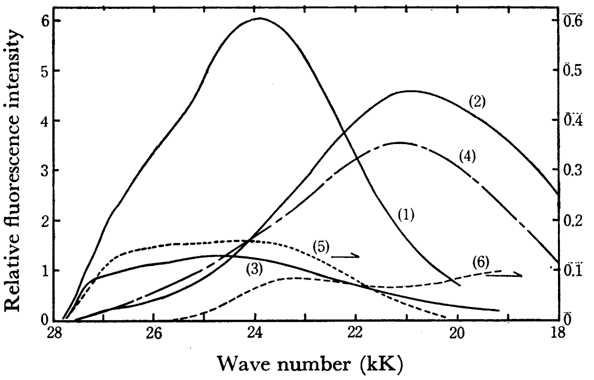

Fig. 4. Fluorescence spectra of the doped PVCz films. Excitation wavelength; 313 or 334 mμ, film thickness; 1 μ, atmosphere; air. (1) undoped, (2) doped with DMTP, (3) DAN, (4) TMPD, (5) TCNE, and (6) PNA.

concerning the electronic interaction between PVCz and a dopant molecule is necessary for understanding the photoconductive properties in doped films, so the fluorescence spectra of doped films excited by 313 or 334 mμ light were measured; they are shown in Fig. 4.

In a film doped with carbazole, the fluorescence spectrum was the same as that of an undoped film, no significant quenching of fluorescence being observed. When PVCz was doped with anthracene or perylene, energy transfer occurred from the excited singlet state of a carbazole chromophor of PVCz to the dopant molecule,[8] and the fluorescence of PVCz was significantly quenched and much fluorescence was emitted by the dopant. For instance, in films doped with 0.3 or 1.4 mol% of perylene the fluorescence of PVCz was quenched by a factor of 6 or 15 respectively.

The fluorescence of perylene in three films with the same doping amount was examined by directly exciting a perylene molecule with 405 mμ light. The films examined were a PVCz film, an *N*-vinylcarbazole (VCz)–vinyl acetate copolymer (VCz 81 mol%) film, and a polystyrene film. The relative intensities of the total fluorescence emission of perylene were as follows: a polystyrene film, 1.0; a VCz-vinyl acetate copolymer film, 0.92, and a PVCz film, 0.82. Thus, the intensity of the total fluorescence emission of perylene doped in a PVCz film is a little smaller than that in a polystyrene film. There may be some interaction between the excited molecule of perylene and a PVCz molecule.

In a film doped with TCNE or DAN, the fluorescence of PVCz was quenched by a factor of 30 in the case of TCNE or by one of 5 in the case of DAN, and no new emission band was observed. In a film doped with TMPD, DMTP, or PNA, the fluorescence of PVCz was quenched by a factor of from 10 to 100 and a new broad emission band was observed at about 21000 cm^{-1}. TMPD being a strong electron donor, the fluorescence of an exciplex between TMPD and perylene[9] or α-methylnaphthalene[10] has been observed in the same wavelength region. The new broad emission band may, therefore, be attributed to the fluorescence of the exciplex. The quenching of the fluorescence of PVCz in a film doped with DAN seems to be due to a similar process. A new broad emission band at about 21000 cm^{-1} in a film doped with DMTP may be attributed to the fluorescence of an exciplex. A similar emission band has been reported in the PVCz–DMTP system in solution.[11] In a film doped with PNA, the fluorescence of PVCz was quenched almost completely and a new weak emission band was observed in the visible region. As the ionization potential of gaseous PNA is 8.85 eV,[12] it is probable that PNA acts as a weak electron acceptor to PVCz. The new emission band may be due to the formation of an exciplex.

Discussion

It is useful to know the relative energy levels of the highest occupied and the lowest unoccupied π molecular orbitals of both the dopants and PVCz in understanding the photo and dark conductivities of the doped films. The dopants used in the present study are molecules with many π electrons, the gaseous ionization potentials of which have been measured by various methods.[12] These values of ionization potential were

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[8] K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa, The 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1970, Preprint 1-142; W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

[9] H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **67**, 791 (1963).

[10] N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **40**, 451 (1967).

[11] Y. Yamamoto, K. Tanaka, T. Omiti, M. Ooka, and T. Nishijima, The first Symposium on Charge Transfer Complex, Nagoya, June, 1969, Preprint p. 105.

[12] F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiely & Sons, Inc., New York (1967), p. 669.

used as a measure of the highest occupied π molecular orbital. The energy level of the lowest unoccupied π molecular orbital was estimated from the energy of the lowest absorption band, which may be attributed to the transition from the highest occupied to the lowest unoccupied π molecular orbitals except in the case of PNA. The lowest absorption band of PNA is due to the intramolecular CT band.[7] The energy levels of both dopants and PVCz thus obtained are shown in Fig. 5. From Fig. 5, the dopants used in this study may be grouped into three categories: donor, acceptor, and neutral. The photoconductive properties and fluorescence spectra of doped films may also be classified into these three groups.

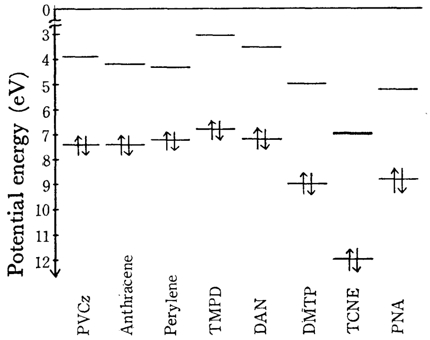

Fig. 5. Relative energy levels of the highest occupied and the lowest unoccupied π molecular orbitals of the dopant molecules and of PVCz.

Donors (TMPD and DAN). Films doped with these donors are characterized by the following three points; a significant decrease in the photocurrents ($i^+_{\text{ph}}=i^-_{\text{ph}}$) in all the wavelength regions, the disappearance of the superlinear dependence of i^+_{ph} on the applied voltage, and a large activation energy of the photocurrent in the high-temperature range.

As the formation of an exciplex $(\text{PVCz}^-\cdots\text{D}^+)^*$ is clear from the fluorescence spectra, the following Eqs., (1) and (2), are conceivable as carrier generation processes.

$$\text{PVCz}^* + \text{D} \longrightarrow (\text{PVCz}^-\cdots\text{D}^+)^* \longrightarrow \text{PVCz}^- + \text{D}^+ \qquad (1)$$

$$\text{D}^+ + \text{PVCz (or PVCz}^*) \longrightarrow \text{D} + \text{PVCz}^+ \qquad (2)$$

where D is a donor molecule; $(\text{PVCz}^-\cdots\text{D}^+)^*$, an exciplex; D^+, an immobile cation of a donor, and PVCz^- and PVCz^+, ion radicals of PVCz (*i.e.*, mobile charge carriers). Equation (1) shows the ionization of an exciplex into a mobile carrier. Equation (2) shows the excitation of an electron from PVCz (or PVCz*) to an electron acceptor, D^+. A similar process has been presented in order to explain the photoconductive properties of a PVCz film,[3] although in that case PVCz acts as an electron donor. In the present case, excited PVCz molecules acting as electron acceptors, these processes do not seem to occur, judging from the significant decrease in the photocurrent in the doped films. This may be due to the ease of recombination between PVCz^- and D^+ in Eq. (1), probably because of the small electron mobility in PVCz films. If so, the formation of an exciplex may have only the effect of decreasing the efficiency of the extrinsic carrier generation through the reduction of the life-time of the excited singlet state of PVCz.

Figure 5 suggests that the highest occupied π molecular orbital of a donor may act as a hole trap level and may reduce the effective hole mobility significantly. Both the increase in the ΔE_{ph} value and the disappearance of the superlinear dependence of i^+_{ph} on the applied voltage can be explained in terms of this hole trapping effect of a donor.

Acceptors (TCNE, DMTP, and PNA). In a film doped with TCNE, a sensitization of the photocurrent was observed in the absorption region of PVCz as well as in the CT absorption region. The apparent quantum yield of the photocurrent was determined as the ratio of the number of electrons flowing in the external circuit to the number of the photons absorbed by the film. It was in the order of 10^{-3}—10^{-2} at the CT bands and in that of $\sim 10^{-4}$ in the UV region. The former is much higher than the latter. The carrier generation *via* the excited CT state, such as that presented by the following equations, seems to contribute considerably to the photocurrent:

$$\begin{array}{ccc} \text{PVCz}^* + \text{TCNE} & \longrightarrow & (\text{PVCz}^+\cdots\text{TCNE}^-)^* \\ (\text{PVCz}\cdots\text{TCNE}) & \overset{h\nu_{\text{CT}}}{\nearrow} & \downarrow \\ & & \text{PVCz}^+ + \text{TCNE}^- \end{array} \qquad (3)$$

$$\text{TCNE}^- + \text{PVCz}^* \longrightarrow \text{TCNE} + \text{PVCz}^- \qquad (4)$$

The film doped with TCNE showed an ESR signal even in the dark. This ESR signal was enhanced a little by illumination both with UV light and with visible light. The ESR signal must be due to the radical ion of TCNE or PVCz. This supports the carrier generation represented by Eqs. (3) and (4).

Although the doping of DMTP had no effect on the photocurrent in the visible region, a significant influence was observed on the photocurrent in the absorption region of PVCz. Both the peak photocurrent and the steady-state photocurrent in the UV region measured under the conditions which made the space charge effect as small as possible were fairly sensitized by doped DMTP; there was no influence on the other properties of the photocurrent, such as the large value of the $i^+_{\text{ph}}/i^-_{\text{ph}}$ ratio, the spectral dependence, and the superlinearity of i^+_{ph} on the applied voltage. It is clear from the fluorescence spectrum that, in this film, the exciplex $(\text{PVCz}^+\cdots\text{DMTP}^-)^*$ is formed with a good efficiency by the UV light illumination in spite of the small concentration of DMTP. The exciplex thus formed seems to be responsible for the chemical sensitization of the photocurrent. The field-assisted thermal dissociation of the exciplex $(\text{PVCz}^+\cdots\text{A}^-)^*$ assumed in the previous paper as an extrinsic carrier generation mechanism in a PVCz film must be a primary carrier generation process under UV illumination in this doped film. This is represented by the following Eqs., (5) and (6):

$$\text{PVCz}^* + \text{DMTP} \longrightarrow (\text{PVCz}^+\cdots\text{DMTP}^-)^* \longrightarrow \text{PVCz}^+ + \text{DMTP}^- \qquad (5)$$

$$\text{PVCz}^* + \text{DMTP}^- \longrightarrow \text{PVCz}^- + \text{DMTP} \qquad (6)$$

In the PNA doped film the photocurrent ($i^{+}_{\rm ph}$) decreased significantly in the UV region, although the exciplex seemed to be formed. Although the reason for this is not clear, it is conceivable that this can be attributed to the effect of the product of the hydrogen abstracting reaction of PNA[13] or to the presence of a small amount of an impurity such as *p*-diaminobenzene, a strong donor, in PNA.

Neutral Materials (Carbazole, Anthracene, and Perylene). Doping of carbazole had no effect on either the photocurrent or the fluorescence spectrum of PVCz.

In a film doped with anthracene or perylene (doping amount, 1—3 mol%), the fluorescence of PVCz was quenched by a factor of from 10 to 30, while the photocurrent in the absorption region of PVCz decreased by a factor of from 2 to 7. Judging from the quenching of the fluorescence of PVCz, the lifetime of the singlet exciton of PVCz and, consequently, the number of the carbazole rings covered with the singlet exciton during its lifetime may be estimated to decrease by a factor of from 10 to 30 as compared with the case of the undoped film. Therefore, in the doped film the efficiency of extrinsic carrier generation will decrease by the same factor. The decrease in the photocurrent in the absorption region of PVCz was, however, much smaller than the decrease presumed from the degree of the fluorescence quenching. This may be due to the contribution of carrier generation through the excited state of the dopant molecule.

In the doped film, the sensitized photocurrent was observed in the proper absorption region of anthracene or perylene. The apparent quantum yield of this photocurrent was from a tenth to a fifth of that of the photocurrent in the proper absorption region in a PVCz film (the quantum yield of PVCz in this region is, for instance, 1×10^{-4} for $i^{+}_{\rm ph}$ at 330 mμ under 35000 V/cm in the film of 15 μ thick). Some interaction between the dopant molecule in the excited state and PVCz in the ground state, which is probable from the fluorescence spectra mentioned above, may be responsible for the photocurrent sensitized spectrally with anthracene or perylene.

Doped anthracene or perylene may be expected from Fig. 5 to act as a hole trap center It has been reported that, in an anthracene single crystal doped with tetracene, the dopant molecule acts as a hole trap center.[14] Such a trapping effect by the dopant was not, however, observed in the film doped with anthracene or perylene.

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