2324 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2324—2331 (1973) [Vol. 46, No. 8

The Photoconductivity of Poly(*N*-vinylcarbazole). III. Photoconductivity in a Sandwich-type Cell.[1]

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(Received March 21, 1972)

Photoconductivity in a sandwich-type cell of a PVCz film was investigated in a high vacuum and in the air. A large photocurrent was observed in the π–π^* absorption region and a small photocurrent in the visible region. The former showed the following interesting points in its behavior. In low applied fields, no difference was found between the photoconductivity with positive-electrode illumination and that with negative-electrode illumination. In moderate or high fields, however, the photoconductivity with positive-electrode illumination was significantly different from that with negative-electrode illumination. The former showed a superlinear dependence on the applied field (consequently, $i_{\mathrm{ph}}^+ \gg i_{\mathrm{ph}}^-$) and a spectral response coinciding with the absorption spectrum. This photoconductive behavior was explained by assuming the mechanism of carrier generation, namely, the field-assisted thermal dissociation of exciplexes and the detrapping of trapped carriers by singlet excitons. Carriers are supposed to migrate through the overlap of π-electrons of neighboring carbazyl rings in the same polymer chain.

Many investigations of the photoconductive properties of poly-*N*-vinylcarbazole (PVCz) have been reported in recent years.[2] Most of them, however, have been carried out in the air. It is well known that ambient oxygen affects the photoconductive properties of molecular crystals.[3] It is, therefore, necessary to investigate the photoconductive properties of PVCz in a high vacuum. In a previous paper the present authors reported on the photoconductivity in a surface-type cell, especially the effect of ambient oxygen on the photoconductivity and the effect of the pre-irradiation of UV light or γ-rays.[4] In the present investigation the authors studied the photoconductivity in a sandwich-type cell of a fresh film of PVCz in a high vacuum (10^{-7} mmHg) as well as in the air.

Experimental

The method of preparing a sandwich-type cell of a PVCz film (area of electrode: 1 cm^2) and the method of electrical measurement were described in the previous paper.[5] A 500W xenon lamp was used as the light source; it was monochromatized by a grating monochromator. The purity of the monochromatic light was 5–10 mμ in the half width; its intensity was changed by means of neutral filters. The light intensity was measured by means of a thermopile (Kipp and Zonen CA 1) or an actinometer by the use of potassium ferrioxalate. The following data were taken for a fresh cell which had stood for several hours in the dark under an applied DC voltage.

Results

Unless otherwise noted, the results were obtained in a high vacuum with freshly cast films 15 μ thick. Although an asymmetrical Metal-PVCz-Nesa sandwich-type cell was used for the following experiments, a symmetrical Au-PVCz-Au sandwich-type cell showed similar results.

Time Dependence of Photocurrent. The response curves of the photocurrent changed with both the applied voltage and the light wavelength. Representative response curves (Types A, B and C) are illustrated in Fig. 1. In low applied fields, the illumination with the weakly-absorbed light ($\lambda > 360$ mμ) induced a photocurrent of the A type, while the illumination with the strongly-absorbed light ($\lambda < 360$ mμ) induced that of the B type. In the latter case, the difference in magnitude between the peak and the steady-state photocurrents becomes smaller with an increase in the applied voltage. The photoresponse curve of the B type seems to be attributable to some effect of non-homogeneously-distributed space charges which are built up by the illumination with the strongly-absorbed light.

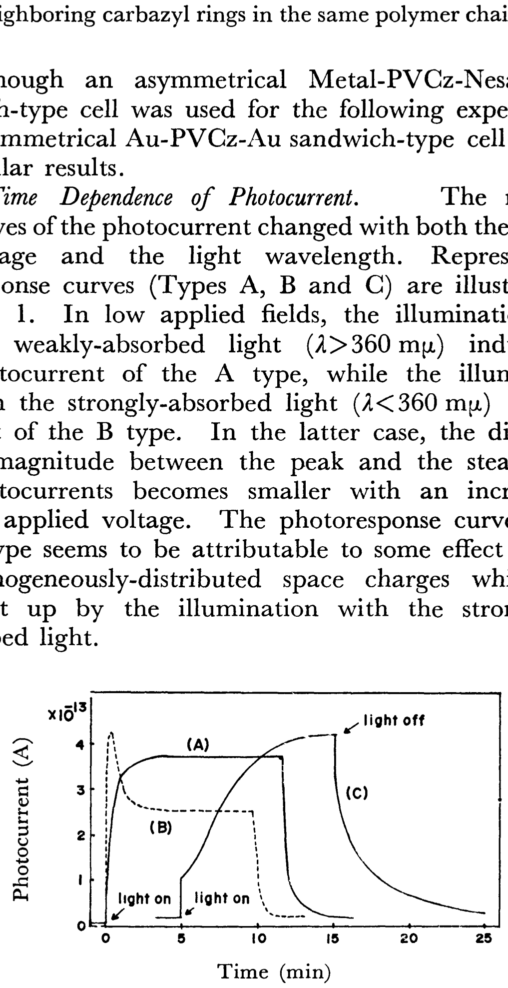

Fig. 1. Representative photoresponse curves in a PVCz sandwich-type cell (Types A, B and C).

In middle applied fields as large as 35000 V/cm, with negative-electrode illumination a photoresponse curve of the B type was observed only at 300—310 mμ. On the other hand, with positive-electrode illumination it was still observed at 270—340 mμ. In high applied fields as large as 150000 V/cm, every photoresponse curve, with one exception, belonged to the A type, and the response times of the rise and decay curves of the

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[1] The experimental results in this paper were presented at the 18th annual meeting of the Society of Polymer Science, Japan Kyoto, May, 1969.

[2] References (1)～(9) of part 1 of this series (see Ref. (4)).

[3] S. Sakai, M. Yoshida, S. Tanaka, H. Mitsudo, and Y. Ooshika, *J. Phys. Chem. Solids*, **28**, 1913 (1967). I. Nakada a H. Kaiyoh, *J. Phys. Soc. Japan*, **17**, 93 (1962). A. Bree and L. E. Lyons, *J. Chem. Soc.*, **1960**, 5179.

[4] K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 1948 (1973).

[5] K. Okamoto, S. Kusabayashi, and H. Mikawa, *ibid.*, **46**, 1953 (1973).

photocurrent were too small to be measured by means of a vibrating-reed electrometer (below 1 sec). The illumination of 230—280 mμ or 350—370 mμ light on a positive electrode or of 350—360 mμ light on a negative electrode induced a photocurrent consisting of two components with different response times (C type), as is shown in Fig. 1. One has a very small response time (below 1 sec), and the other, a fairly large one (5—20 min). Similar behavior was observed in the decay part of this photocurrent. The subsequent re-illumination of the same light induced a photocurrent with the same behavior and also consisting of two components.

The results to be presented below were obtained for the steady-state values of the photocurrent, unless otherwise noted.

Voltage Dependence of Photocurrent. Figure 2 shows the voltage dependence of the photocurrent. In applied fields lower than 2000 V/cm the photocurrent was proportional to the applied voltage regardless of either the polarity of the illuminated electrode or the wavelength of the illuminating light, although some photocurrent (photovoltaic current) was observed without any applied voltage. In low fields the observed photocurrent apparently consists of both a photovoltaic current and a true photocurrent.

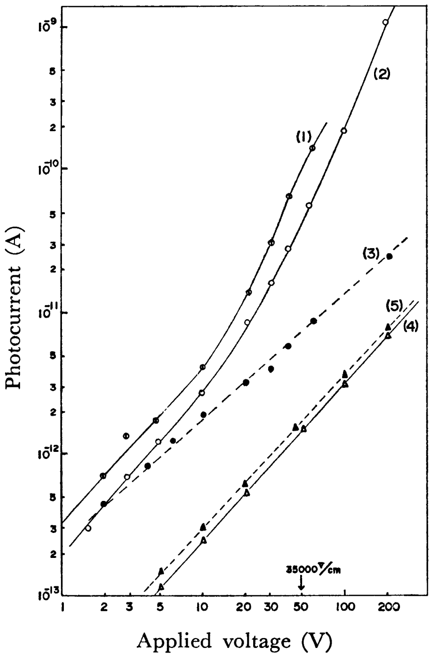

Fig. 2. Voltage dependence of photocurrent in an Ag-PVCz-Nesa sandwich-type cell. In high vacuum with nesa electrode illumination.
(1) peak value of $i_{\mathrm{ph}}{}^{+}$ at 330 mμ, (2) steady state value of $_{\mathrm{ph}}{}^{+}$ at 330 mμ, (3) steady state value of $i_{\mathrm{ph}}{}^{-}$ at 330 mμ, (4) $i_{\mathrm{ph}}{}^{+}$ at 500 mμ, and (5) $i_{\mathrm{ph}}{}^{-}$ at 500 mμ.

In applied fields higher than about 7000 V/cm the voltage dependence of the photocurrent, however, varied with both the polarity of the illuminated electrode and the wavelength. In the case of negative-electrode illumination the photo-current (abbreviated to $i_{\mathrm{ph}}{}^{-}$) was proportional to the applied voltage in every wavelength region over the whole range of voltage applied (0—150000 V/cm). On the other hand, in the case of positive electrode illumination the photocurrent (abbreviated to $i_{\mathrm{ph}}{}^{+}$) changed with 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 longer than 360 mμ. It should be noted that the wavelength of 360 mμ corresponds to the absorption edge of a film 15 μ thick. The superlinearity of the photocurrent on the applied voltage was observed not only for the steady-state photocurrent, but also for the peak value of the photocurrent of the B type, as is shown by Curve (1) in Fig. 2. This voltage dependence of the photocurrent was not affected by the electrode materials, such as Au, Ag, Cu, Al, and nesa coating.

Light-intensity Dependence of Photocurrent. The photocurrent was always proportional to the light intensity (10^{12}—10^{14} photons/cm^2 s) regardless of the applied voltage, the wavelength (300—600 mμ), the polarity of the illuminated electrode, and the ambient oxygen, as is shown in Fig. 3. In a surface-type cell the photocurrent showed a linear dependence on the light intensity in a high vacuum and a sublinear dependence in the air. This lowering of the light-intensity dependence of the photocurrent was attributed to the introduction of some shallow hole trap levels by the air.[4] The effect of the hole trap levels due to oxygen molecules in the air may not be significant in a sandwich type cell.

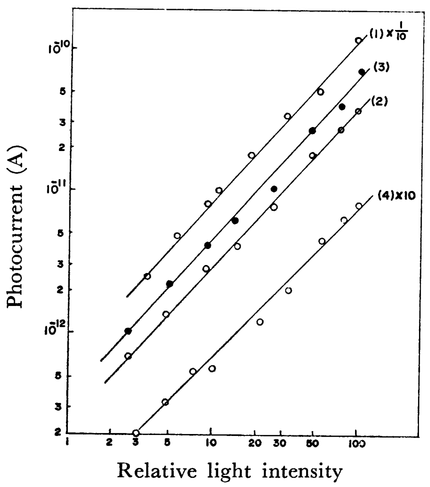

Fig. 3. Light intensity dependence of photocurrent in an Au-PVCz-Nesa sandwich-type cell. With positive Au electrode illumination.
(1) 350 mμ, 150000 V/cm in high vacuum; (2) 350 mμ, 35000 V/cm in high vacuum; (3) 350 mμ, 35000 V/cm in the air and (4) 450 mμ, 35000 V/cm in high vacuum.

Spectral Dependence of Photocurrent. The spectral dependence of the photocurrent shown in Figs. 4 and 8 was obtained by normalizing the observed photocurrent values to the values for the light intensity of 2×10^{13} photons/cm^2 s according to the light-intensity dependence. The spectral dependence of the photocurrent varied with the polarity of the illuminated electrode, the applied voltage, and the film thickness, but it was not affected by either air or the electrode materials. As is shown by the dotted line in Fig. 4,

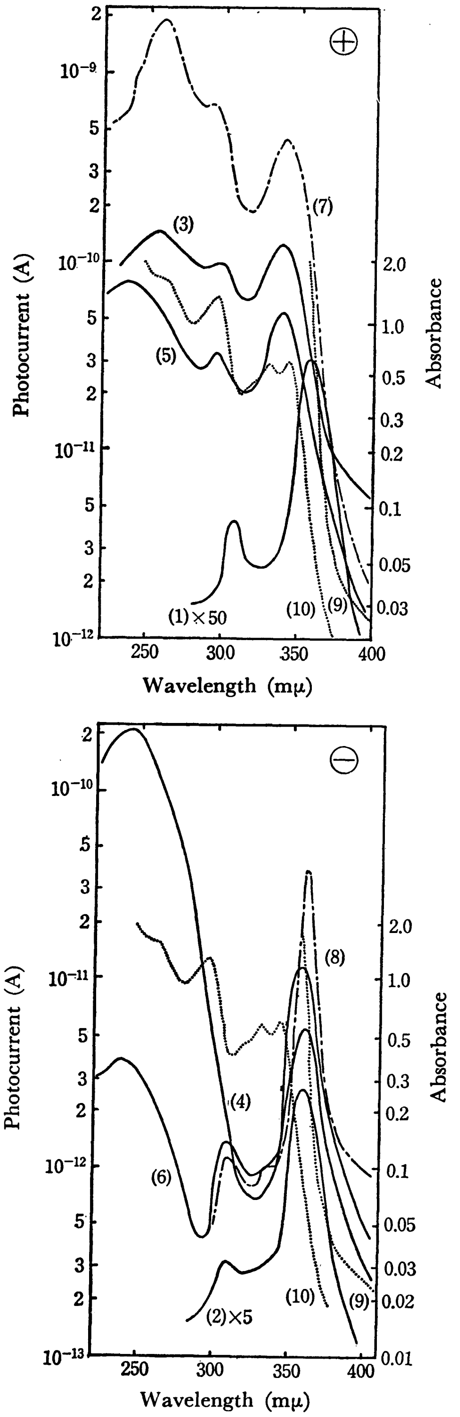

Fig. 4. Spectral dependence of photocurrent in an Au-PVCz-Nesa sandwich-type cell. Film thickness 15 μ. With positive Au electrode illumination; (1) 2 V (3) 50 V and (5) 50 V. With negative Au electrode illumination; (2) 2 V (4) 50 V and (6) 50 V. With positive nesa electrode illumination; (7) 200 V. With negative nesa electrode illumination; (8) 200 V. (1)∼(4) and (7)∼(8), in high vacuum. (5) and (6), in the air. (9) absorption spectrum of a PVCz film 15 μ thick. (10) absorption spectrum of a PVCz film about 1 μ thick.

the absorption spectrum of PVCz has its absorption maxima at 344.8, 331.8, 297, and 262.8 mμ and its absorption minima at 338, 312, and 282 mμ.

In low fields no difference was observed between i_{ph}^+ and i_{ph}^- either in magnitude or in the positions of the peaks and the minima. The photocurrent peaks were observed at 360, 310, and 250 mμ, and the photocurrent minima, at 330 and 290 mμ. This spectral dependence of the photocurrent corresponds inversely to the absorption spectrum except for the 250 mμ peak. This behavior is similar to that reported by Klöpffer *et al.*.[6] The 360-mμ photocurrent peak was observed at the absorption edge. The 330-mμ photocurrent minimum was observed in the region of the 344.8- and 331.8-mμ absorption peaks, which were unresolved in the photocurrent spectrum, probably because of both the fairly large half-width of the monochromatic light and the small difference in the extinction coefficients in this region.

In the middle applied fields as large as 35000 V/cm, a marked difference of photocurrent was observed both in magnitude and in the positions of the photocurrent peaks and minima, depending on whether the positive or the negative electrode was illuminated. With negative-electrode illumination the spectral dependence of the photocurrent was similar to the case of the low applied field; that is, it corresponded inversely to the absorption spectrum. With positive-electrode illumination, however, the photocurrent peaks shifted to a shorter wavelength and were observed at 340, 295—300 and 240—250 mμ, while the photocurrent minima were observed at 315 and 285 mμ. The spectral dependence of i_{ph}^+ thus corresponded just to the absorption spectrum. The magnitude of i_{ph}^+ in the UV region was 20—100 times larger than the corresponding value of i_{ph}^-. This is apparently attributable to the superlinear dependence of i_{ph}^+ on the applied voltage in the middle and high fields.

In the high fields as large as 150000 V/cm the spectral dependence of the photocurrent was the same as in the case of a middle applied field. The i_{ph}^+/i_{ph}^- ratio in the UV region was 70—500. This value of the ratio is 3—10 times larger than that in the middle applied fields. These results were obtained for a film 15 μ thick. As is shown in Fig. 8, in a thick film (0.5 mm thick) the 360 mμ photocurrent peak for the film 15 μ thick shifted to 370—380 mμ, which corresponds to the absorption edge of the thick film.

The above-mentioned spectral dependence of i_{ph}^+ is a new observation, one very different from those reported by others.[6]

In a high vacuum with a negative illuminated metal electrode a large photocurrent with no activation energy was observed in the region shorter than 300 mμ, as is shown by Curve (4) in Fig. 4. This is attributable to the photoemission current from the electrode metal into a high vacuum, independent of PVCz.

Temperature Dependence of Photocurrent. Figure 5 shows the temperature dependence of the photocurrent. Log i_{ph} *vs* $1/T$ plots gave straight lines over the whole temperature range (20—160 °C).

In a middle field, 35000 V/cm, the activation energy of the photocurrent (ΔE_{ph} in the equation: $i_{ph} \propto \exp(-\Delta E_{ph}/kT)$) was 0.07—0.15 eV in the visible

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[6] H. Bauser and W. Klöpffer, *Chem. Phys. Lett.*, **7**, 137 (1970); *Kolloid Z. Z. Polym.*, **241**, 1026 (1970). M. Hayashi, M. Kuroda, T. Imura, and A. Inami, *Kobunshikagaku*, **21**, 577 (1964).

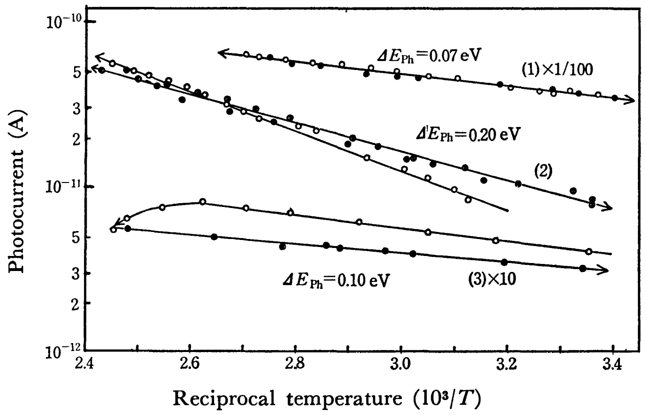

Fig. 5. Temperature dependence of photocurrent in an Au-PVCz-Nesa sandwich-type cell. With positive-electrode illumination in high vacuum.
(1) 350 mμ (Nesa), 150000 V/cm. (2) 360 mμ (Au), 35000 V/cm. (3) 450 mμ (Au), 35000 V/cm.
○; the first heating run. ●; the first cooling run. ◐; the second heating run.

region and 0.18—0.22 eV in the UV region. The latter is larger than the former by about 0.09 eV. In a high field, 150000 V/cm, ΔE_{ph} in the UV region was 0.07—0.10 eV, smaller by about 0.11 eV than the corresponding ΔE_{ph} value at 35000 V/cm.

There is no significant difference between the photoconductive properties mentioned above in a high vacuum and those in the air.

Photovoltaic Current. Even without applied voltage a fairly large photocurrent was observed in a short circuit, the spectral response of which is shown in Figs. 6(a) and (b). In the cell which had not been exposed to air after the evaporation of a metal electrode in a high vacuum, the photocurrent always flowed in the bulk from a metal electrode to a nesa electrode, regardless of whether the nesa or the metal electrode was illuminated. This photocurrent cannot be explained by the Dember effect, the difference in the carrier mobilities, but seems to be caused by a photovoltaic effect resulting from the contact interface between the electrode and the PVCz film. The authors called this photocurrent a "photovoltaic current."

The photovoltaic current is changed irreversibly by the introduction of air. In the air, with metal electrode illumination the photovoltaic current flowed in the bulk from a metal to a nesa electrode, as in the case of a high vacuum. With nesa electrode illumination, however, it flowed oppositely in the region shorter than 360 mμ, as is shown in Fig. 6(b). Furthermore, the photovoltaic current in the air was much smaller than that in high vacuum. When a cell exposed once to air after the evaporation of an electrode was put back into a high vacuum, the photovoltaic current was not restored to its original value.

It seems that the phenomena mentioned above can be interpreted by supposing that there is a large potential barrier at the interface between a metal electrode and a PVCz film, such as the well-known barrier in a metal—P type semiconductor system.[7] This potential barrier may determine the photovoltaic current in a high vacuum. The potential barrier is lowered by the air, as is observed in a metal—P type semiconductor system. If so, in the air the photovoltaic current seems to be determined mainly by the Dember effect.

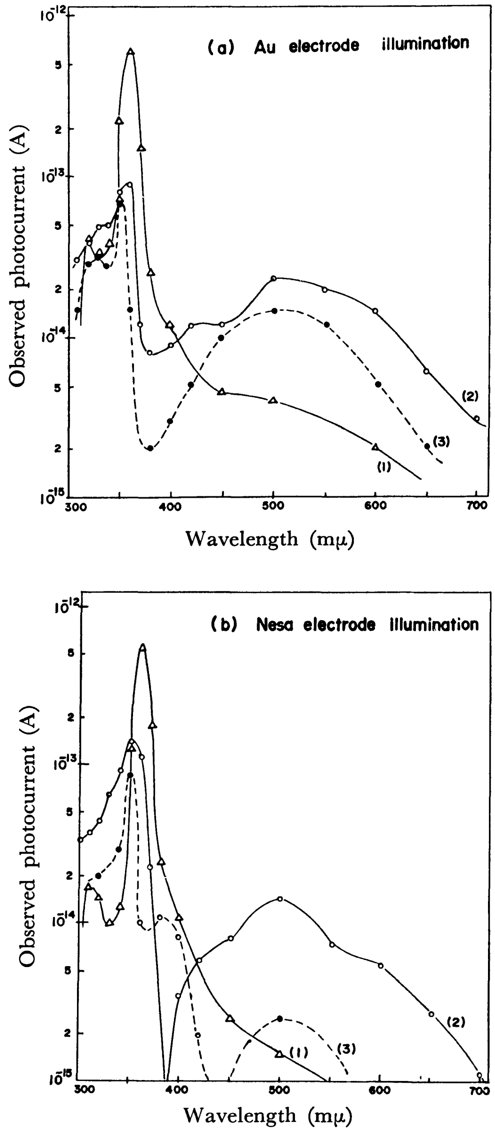

Fig. 6. Photovoltaic current in an Au-PVCz-Nesa sandwich-type cell.
(a) Au electrode illumination. The photovoltaic current always flows from Au to nesa in the bulk. (1) in high vacuum, for the cell which has not been exposed to air after the evaporation of an Au electrode. (2) in the air. (3) in high vacuum after exposing the cell to air.
(b) Nesa electrode illumination. (1) in high vacuum, the photovoltaic current flows from Au to nesa in the bulk. (2) in the air, from nesa to Au at $\lambda<380$ mμ and from Au to nesa at $\lambda>400$ mμ. (3) in high vacuum after exposing the cell to air, from nesa to Au at $\lambda<420$ mμ and from Au to nesa at $\lambda>420$ mμ.

Hole Injection into a PVCz Film from a Metal Electrode. The photoemission of holes from various metals (Au, Al and Cu) into a PVCz film has been observed by Lakatos *et al.*[8] Hole emission was observed also in an

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[7] L. E. Lyons, "Physics and Chemistry of the Organic Solid State," Vol. 1. ed. by D. Fox, M. M. Labes and A. Weissberger, Interscience Publishers, New York (1963), p. 788.

[8] A. I. Lakatos and J. Mort, *Phys. Rev. Lett.*, **21**, 1444 (1968).

Au-PVCz-Nesa sandwich-type cell and was found to be significantly affected by the air. When a cell was not exposed to air after the evaporation of a gold electrode in a high vacuum, no photocurrent due to hole injection from the gold electrode was observed. The photocurrent in the visible and the near IR regions with the gold positive electrode showed values similar to those of the negative gold electrode as is shown in Fig. 7. If a cell was exposed to air after the evaporation of a gold electrode in a high vacuum, it showed a fairly large current due to hole emission both in the air and in a high vacuum; that is, the photocurrent in the visible and the near IR regions with the positive gold electrode increased significantly and was much larger than the photocurrent with the negative gold electrode, as shown in Fig. 7.

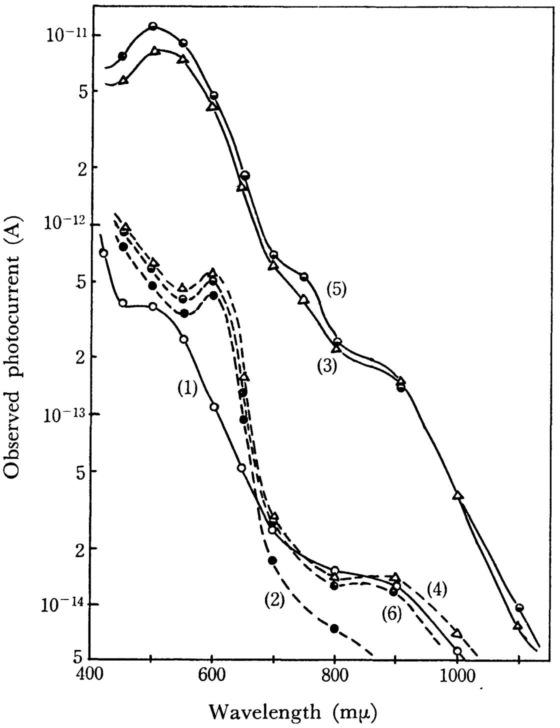

Fig. 7. Effect of air on photocurrent in the visible and the near IR regions in an Au-PVCz-Nesa sandwich-type cell.
With illuminated Au electrode biased positively (1, 3 and 5) or negatively (2, 4 and 6), under 35000 V/cm. (1) and (2); in high vacuum, for the cell which has not been exposed to air after the evaporation of an Au electrode. (3) and (4); in the air. (5) and (6); in high vacuum, for the cell having been exposed to air.

The above-mentioned effect of air on the hole emission current can probably be interpreted in terms of a decrease in the contact potential barrier, just as in the case of the photovoltaic current discussed above.

Effect of the Crystallinity on Photocurrent. Untreated PVCz has poor crystallinity, but the crystallinity was improved by appropriate heat-treatment.[9] The relation between the crystallinity and the photoconductivity was studied. The powder of the polymer was compressed to a disk (1 cm in diameter and 2—3 mm thick), which was then hot-pressed under various conditions to a film with varied crystallinity. Gold semitransparent electrodes were evaporated on both sides of the film. The photocurrent was measured for the Au-PVCz-Au sandwich-type cell thus obtained; it is shown in Fig. 8 and in Table 1. Judging from the crystalline peak at $2\theta=8°15'$[9,10] in the X-ray diffraction curves shown in Fig. 9, the I film is highly crystalline, while II is moderately and III, poorly so.

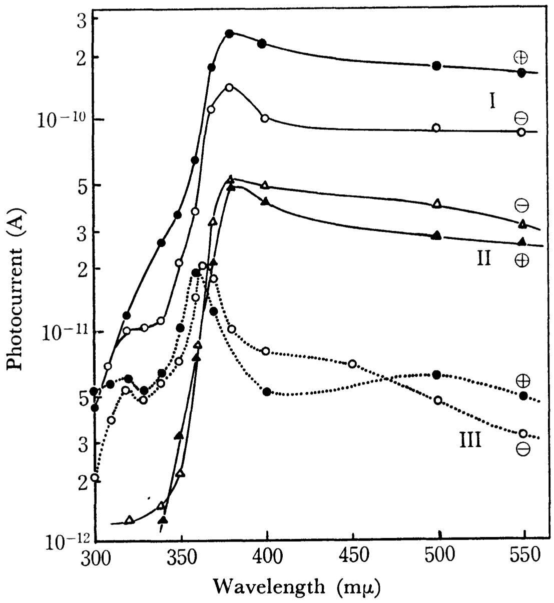

Fig. 8. Effect of the crystallinity of a PVCz film on photocurrent. In high vacuum, 8000 V/cm. ⊕; positive-electrode illumination, ⊖; negative-electrode illumination.
I, a film annealed under a hot-press (240° C, 150 kg/cm², 40 min), highly crystalline, 0.5 mm thick. II, a film annealed under a hot press (240 °C, 100 kg/cm², 15 min), moderately crystalline, 0.4 mm thick. III, a film cast from a benzene solution, poorly crystalline, 0.07 mm thick.

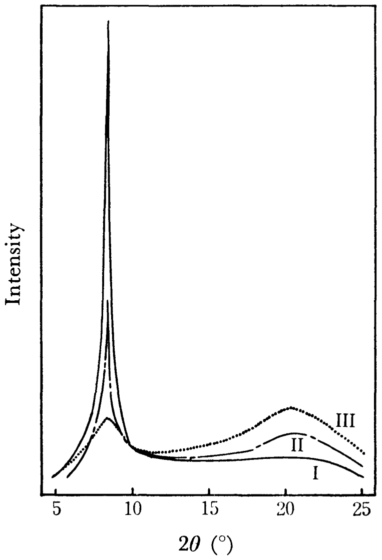

Fig. 9. X-ray diffraction patterns of PVCz films. I, II and III are the same films as described in Fig. 8 and Table 1.

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[9] A. Kimura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa, and N. Kasai, *J. Polym. Sci. A-2*, **8**, 643 (1970).

[10] R. G. Crystal, *Macromolecules*, **4**, 379 (1971).

The magnitude of the photocurrent could not be compared directly in these three kinds of films because the spectral response curves changed slightly with the film thickness, as is shown in Fig. 8. As the red shift of the photocurrent peak in the longer wavelength π–π^* absorption region is mainly due to the change in the absorption edge of a film with the film thickness, the magnitude of the photocurrent maximum at this wavelength was compared in order to examine the correlation between the crystallinity and the photocurrent. As is shown in Table 1, the higher the crystallinity of a film, the larger the photocurrent.

Although the results shown in Table 1 may not be attributable to only the difference in crystallinity because of the effect of heat-treatment on the concentration of impurity in a film, they seem to suggest a correlation between the crystallinity and the photoconductivity. A similar correlation has been reported for the γ-ray induced current in polyethylene films.[11]

TABLE 1. EFFECT OF THE CRYSTALLINITY OF PVCz FILMS ON PHOTOCURRENT

Film No.	Thickness (mm)	Crystallinity	Absorption edge (mμ)	Photocurrent[a]	
				i_{ph}^+	i_{ph}^-
III	0.5	very good	380	7.4	12.5
III	0.4	moderate	380	2.6	2.4
III	0.07	poor	360	1	1

a) Relative value of photocurrent at the peak wavelength, film III being a standard. Under 8000 V/cm in high vacuum.

Discussion

Sharp reported on the photoconductivity of *N*-isopropylcarbazole, a model compound of PVCz.[12] No photocurrent was observed in the π–π^* absorption region longer than 280 mμ, although some intrinsic photoconduction was observed in the region shorter than 280 mμ. Furthermore, i_{ph}^- was larger than i_{ph}^+. An acceptor such as picryl chloride does not sensitize the photocurrent and acts only as a trapping center for an electron, the majority carrier. It has also been reported that the photoconductivities of *N*-vinylcarbazole and some alkylcarbazoles are smaller than that of PVCz, and that the light in the lower π–π^* absorption region is not effective for photoconduction.[13]

As is shown in Fig. 4, PVCz shows, however, a large photocurrent both in the lower and higher π–π^* absorption regions as well as a small photocurrent in the visible region. Furthermore, i_{ph}^+ is much larger than i_{ph}^- in moderate and high applied fields and a hole is expected to be the majority carrier. These photoconductive properties of PVCz are thus in sharp contrast with the photoconductivity of the related compounds.

Carrier Generation. The photocurrent in the visible region must be due to the optical reexcitation of trapped carriers, as has been reported previously.[4] Now, we are interested in carrier generation in the π–π^* absorption region of PVCz.

We have found that PVCz, a fairly strong electron donor, interacts easily even with a very weak electron acceptor, such as dimethyl terephthalate or chloroform, to form a so-called exciplex.[14] This suggests the possibility of the existence of some impurity in a PVCz film, which can form an exciplex under UV illumination. As the singlet exciton created by the π–π^* absorption in PVCz covers many pendant carbazyl groups during its lifetime,[14,15] a fairly high exciplex-forming efficiency can be expected by the π–π^* excitation. The carrier generation *via* the exciplex may be considered.

$$D^* + A \rightarrow (D^+\cdots A^-)^* \rightarrow D^+ + A^-, \qquad (1)$$

$$A^- + D \text{ or } D^* \rightarrow D^- + A, \qquad (2)$$

where D is the ground state of PVCz; D*, a singlet excited state; A, an impurity with an electron accepting property, and A^-, an impurity anion (immobile). $(D^+\cdots A^-)^*$ are an exciplex, D^+ and D^- are ion radicals of PVCz (*i.e.*, mobile charge carriers). Equation (1) shows the ionization of an exciplex (ion pair) into a mobile carrier ion in a film. Equation (2) shows the excitation of an electron donor (A^-) thermally or by a singlet exciton. The excitations of trapped carriers and/or of acceptors by singlet excitons may also be considered.

$$\begin{aligned} M^+ + D^* &\rightarrow M + D^+, \\ M^- + D^* &\rightarrow M + D^-, \end{aligned} \qquad (3)$$

where M^+ is a trapped hole or an acceptor, and M^-, a trapped electron or a donor. The detrapping of trapped carriers by singlet excitons has been examined in anthracene.[16]

The dissociation of an exciplex (or ion pair) has been discussed in connection with the photoconductivity in aromatic hydrocarbon crystals. The energy required for the separation of an ion pair is evaluated roughly as 0.5 eV for anthracene.[17] The dissociation of an ion pair in a molecular crystal will need a fairly large activation energy. It may usually be difficult for an exciplex to dissociate into free ions in a film with a low dielectric constant. This dissociation may, however, be possible under conditions which reduce the energy required for the separation of an ion pair,—for example, under a strong electric field, as has been proposed by Lyons.[18] The following two kinds of fields[19] may be considered as strong electric fields in a PVCz film: (a) the local field surrounding an ion already produced (or a trapped carrier), and (b) the field near the surface which may act as a part of a diffuse double layer.

In a PVCz sandwich-type cell both carriers are not

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[11] K. Yahagi and K. Shinohara, *J. Appl. Phys.*, **37**, 310 (1966).

[12] J. H. Sharp, *J. Phys. Chem.*, **71**, 2587 (1967).

[13] M. Lardon, E. Lell-Daller, and J. W. Weigl, *Mol. Cryst.* **2**, 241 (1967).

[14] K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa; The 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1969. Preprint 1-142.

[15] W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

[16] M. Pope, J. Burgos and N. Wotherspoon, *Chem. Phys. Lett.*, **12**, 140 (1971).

[17] F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons Inc., New York (1967), p. 349.

[18] L. E. Lyons, *J. Chem. Soc.*, **1957**, 5001.

[19] Ref. 17, p. 392.

replenished with a metal or a nesa electrode.[13,21,22] Both carriers must be discharged at each electrode according to the electroneutral condition. The magnitude of photocurrent will be limited by the smaller value of either the number of holes having reached a negative electrode through the bulk or the number of electrons having reached a positive electrode. For the understanding of the photoconductive behavior, it is important to know how this number changes with the applied voltage, the polarity of the illuminated electrode, or the wavelength of the illuminating light.

If the processes represented by Eqs. (1), (2) and (3) are supposed to be carrier generation processes in the UV region in a PVCz sandwich-type cell, the photoconductive behavior can be explained favorably as follows.

In low applied fields, the exciplex will dissociate into free ions only in the local field surrounding an ion (or a trapped carrier), because the field near the surface will be small. The carriers will also be created by Process (3). In a PVCz film, impurities, A, and trapped carriers (or acceptors) will exist not only at the surface layer but also in the bulk. In homogeneous carrier generation, (1) recombination of the carriers will occur with a lower probability because of the lower concentration of the carriers than that in the case of surface carrier generation; (2) both carriers migrate in the bulk and can contribute to the photocurrent, and (3) space charge effects will be smaller because of the relatively homogeneous distribution of trapped carriers. Therefore, in general, homogeneous carrier generation in the bulk seems to be favored rather than the generation at surface. With an increase in the absorption coefficient of a film, the illuminating light is absorbed only in the region near the surface and the favorable conditions in the homogeneous carrier generation gradually disappear. Therefore, the spectral response of the photocurrent corresponds inversely to the absorption spectrum and the photocurrent peak in the longer wavelength region shows a red shift with an increase in the film thickness, unless there is an additional condition favoring the surface carrier generation. There is no significant difference either in magnitude or in the spectral dependence between i_{ph}^+ and i_{ph}^- in low fields.

When a higher voltage is applied, the field near the surface becomes larger and may be supposed to be large enough to assist the thermal dissociation of an exciplex. With positive-electrode illumination, hole carriers generated will be swept away before recombining with the immobile A^- ion. A mobile electron is generated from an A^- ion by Process (2). Thus, the thermal dissociation of an exciplex assisted by the field near the surface may act as a primary carrier generation process. Therefore, with an increase in applied voltage, significantly more carriers are generated, more favorably in the vicinity of an illuminated positive electrode rather than in the bulk. Consequently the spectral response of the photocurrent corresponds to the absorption spectrum with positive-electrode illumination in moderate and high applied fields. During the migration in the bulk to the opposite negative electrode, the hole carriers are frequently trapped and gradually fill hole traps in the same manner as has been mentioned previously.[4] As a result of the hole traps being filled, the effective mobility of a hole may become larger. With positive-electrode illumination, the number of holes reaching the negative electrode will become significantly larger with the applied voltage;—i_{ph}^+ in the UV region has, therefore, a superlinear dependence on the applied field.

On the other hand, in the case of negative-electrode illumination, most of the hole carriers generated by the same process as in positive-electrode illumination remain near the surface, without discharging at a negative electrode, and recombine with the immobile A^- ion. With negative-electrode illumination, the thermal dissociation of an exciplex assisted by the field near the surface seems not to act as a carrier generation process and the bulk carrier generation seems to be predominant even above a middle applied field. The i_{ph}^- neither shows a superlinear dependence on the applied voltage nor a spectral response corresponding to the absorption spectrum, even in high applied fields.

Photoresponse Curves. With positive-electrode illumination, as the carriers are generated preferentially at the surface, some effect of space charges distributed nonhomogeneously in a film may be more significant than in the case of the negative-electrode illumination. For this reason, a photoresponse curve of the B type is observed with positive-electrode illumination by the UV light, even in middle applied fields.

In high applied fields, the B type is not observed and the C type as well as the A type is observed. This may be explained as follows. At a high applied voltage, the effective hole mobility increases with the filling of hole traps and finally becomes equal to the value of the hole mobility which would be observed in the absence of any traps. With this gradual increase in the effective hole mobility, the photocurrent gradually increases during the illumination. In high fields the homogeneous illumination gives a photoresponse curve of the C type in Fig. 1, while the nonhomogeneous illumination gives an A or C type.

Activation Energy of Photocurrent. As the photocurrent in the visible region is due to the optical reexcitation of the carriers trapped by deep trap levels,[4] no significant activation energy seems to be needed for the carrier generation. The activation energy, ΔE_{ph} (0.07—0.15 eV at 35000 V/cm), in the visible region seems to be the energy required for the carrier migration. In a middle field (35000 V/cm) ΔE_{ph} in the UV region is assumed to be the sum of the activation energy for carrier migration and that for carrier generation. The former is estimated to be less than the value of ΔE_{ph} in the visible region, because under UV illumination a steady-state Fermi level for the hole[20] is lowered much more than in the case of visible illumination. The latter may be the energy required for the field-assisted thermal dissociation of an exciplex. In a high field as large as 150000 V/cm, the value of ΔE_{ph} in the UV region was lowered by about 0.1 eV. This lowering of the ΔE_{ph} value may be due to the filling up of the hole traps mentioned above, and the ΔE_{ph} value observed in high fields may not be the

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20) A. Rose, *RCA Rev.*, **1951**, 362. *Phys. Rev.*, **97**, 322 (1955).

energy required for the carrier migration, but only that required for the carrier generation. The energy required for the field-assisted thermal dissociation of an exciplex may, consequently, be estimated to be about 0.1 eV.

Comparison with Pulse Photoconductivity Data. The transient pulse photocurrent in a PVCz film has been reported on by Regensburger,[21] Szymanski,[22] and Pai.[23] Their results, which were obtained under high applied fields, agree with each other in the following two points. The efficiency of hole carrier generation increases significantly with an increase in the applied field; the hole carrier mobility also increases significantly with both the temperature and the applied field, suggesting that the hole carrier migration process involves the field-assisted thermally-activated jump. These results correspond to the finding of the superlinearity of the voltage dependence of i_{ph}^{+}, which was observed in the steady-state photocurrent in the present investigation. The activation energy for hole carrier generation obtained from the transient measurements is nearly the same as the value (about 0.1 eV) observed in the present steady-state measurements. The activation energy for hole carrier migration obtained from the transient measurement (0.36 eV[23] or 0.4—0.7 eV[21] in air) is much larger than that (about 0.1 eV at 35000 V/cm and nearly zero at 150000 V/cm) observed in the present investigation. This may be attributed to the fact that, under the steady-state conditions, most of the hole traps are filled by holes, while under the conditions of the transient measurements the hole traps remain empty during the experiment.

Carrier Migration. From the X-ray analysis,[9,10] NMR spectra[24,25] and electron diffraction[10] the structure of solid PVCz has been suggested to be as follows. The crystalline nature of PVCz is sensitive to heat treatment. In a specimen stretched under a hot-press, the crystalline diffraction peak at $2\theta=8°15'$ is sharp and strong and the amorphous peak shows an appreciable decrease in its intensity. Thus, an annealed or stretched film is crystalline and takes a pseudo-hexagonal packing structure of a rigid rod-like molecule, with a cross sectional diameter of about 12.6 Å with only a chain-to-chain order. This chain may have isotactic 3/1 and syndiotactic 2/1 helix parts in a stereoblock manner.

From the structure of solid PVCz, it seems most probable that carriers can move primarily along the chain from a carbazyl group to another adjacent carbazyl group, through the overlap of the π-electron systems of carbazyl rings in the same polymer chain. This carrier migration process is supported by the correlation between the crystallinity and the photocurrent and also strongly by the significant decrease in the photocurrent in the copolymers of *N*-vinylcarbazole with a small amount of another monomer, which severs the overlap of the π-electron systems of carbazyl rings in the same polymer chain, thereby significant hindering the migration of the carriers.[26]

The authors wish to acknowledge the financial support of the Fuji Photo Co. for this work.

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21) P. J. Regensburger, *Photochem. Photobio.*, **8**, 429 (1968).

22) A. Szymanski and M. M. Labes, *J. Chem. Phys.*, **50**, 3568 (1969).

23) D. M. Pai, *ibid.*, **52**, 2285 (1970).

24) S. Yoshimoto, Y. Akana, A. Kimura, H. Hirata, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, **1969**, 987.

25) D. J. Williams, *Macromolecules*, **3**, 5602 (1970).

26) K. Okamoto, K. Kato, S. Kusabayashi, and H. Mikawa, This Bulletin, in press.