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The Photoconductivity of Poly(*N*-vinylcarbazole). I. The Photoconductivity in a Surface-type Cell*

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 of poly-*N*-vinylcarbazole in a surface-type cell was measured both in a high vacuum and in the air. Fresh films showed a large photocurrent in the lower π-π^* absorption region and a small photocurrent in the visible region. The threshold of the photocurrent was found at about 600 mμ. By heat treatment or by pre-irradiation with UV-light or γ-ray, the photocurrent increased throughout the spectral region and its threshold shifted to a longer wavelength. Both the dark current and the photocurrent in the visible and the near IR regions must be due to the thermal or optical reexcitation of the trapped carriers. The activation energies of the dark current (0.4—1.3 eV) and the photocurrent (0.06—1.0 eV) differ according to the temperature range, the light wavelength, and the film history (whether fresh film or one of various pre-treated films). The activation energies are needed for carrier migration and can be explained by the "trapping conduction mechanism".

Recently many vinyl polymers with large pendant π-electron systems have been synthesized in expectation of their having good photoconductive properties. These polymer materials will be useful for electrophotography. The polymers synthesized and examined for photoconductivity measurements are poly-*N*-vinylcarba-

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** Present address: Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755.

zole (PVCz),[1-9] polyvinylanthracene,[10,11] polyvinylpyrene,[12] polypyrenylmethylvinylether,[13] polyvinylacridine,[14] and polyacenaphthylene.[15] PVCz is one of the most photoconductive polymers, and it is now being used as a material for electrophotography.

In the present series of papers on the electrical properties of PVCz, the authors have examined the photoconductivity of PVCz purified as far as possible, especially under a high vacuum, for the purpose of clarifying the origin of the photoconductivity of PVCz. These studies can be expected to give us some guiding principles for preparing new photoconductive polymers with high sensitivity.

This paper will deal with the photoconductivity of fresh films in a surface-type cell. The effect of air, heating, or pre-irradiation with UV light or γ-rays will also be investigated.

Experimental

Materials. *N*-Vinylcarbazole was recrystallized three times from methanol and three times from *n*-hexane; it was then polymerized by heating it together with azobisisobutyronitril in benzene at 70 °C for 2 hr. The polymer was purified three times by reprecipitation from benzene–methanol. The molecular weight was determined to be 110000 by means of a membrane osmometer.

Measurements. The following four kinds of films were used.

a) Fresh film. A 0.2 ml portion of a 5 wt% benzene solution of the polymer was placed on a quartz plate (20×25 mm^2), and the solvent was evaporated slowly in the dark under a nitrogen atmosphere. The thickness of the film was determined to be about 15 μ by studying the UV absorption. The film showed an absorption edge at 357 mμ.

b) Film irradiated with UV light. A fresh film was irradiated with UV light in the air for 15 hr, 50 cm distant from a 500 W xenon lamp without a condenser lens.

c) Film irradiated with γ-rays. A fresh film was irradiated with γ-rays (^{60}Co) in the air for 1—50 hr (dose amount; 5×10^4—2×10^6 R).

d) Hot-pressed film. The powder of the polymer was compressed to a disk under a pressure of 80 kg/cm^2 and then hot-pressed at 220—240 °C in the air to a transparent film. There was no difference in either the IR spectrum or the UV spectrum among these four kinds of films. The γ-irradiated film showed a broad ESR signal ($g=2.0$) which was very stable and which did not disappear even after the film has been heated at 100 °C for 2 hr in a high vacuum.

In order to prepare a surface-type cell, Au or Ag comb-type electrodes (50 mm in length and 0.18 mm in electrode distance) were evaporated on the film, and then lead wires were placed in these electrodes by means of silver paste. A high-vacuum evaporation apparatus was prepared to obtain a clean vacuum of the order of 10^{-8} mmHg, according to the method reported by Maruyama *et al.*[16] This enabled us to measure photo- and dark-currents larger than 5×10^{-16} A in a high vacuum at 10—200 °C. The DC conductivity was measured by means of a vibrating-reed electrometer (Takeda Riken TR 84M). A stabilized 500 W xenon lamp was used as the light source; it was monochromatized by means of a prism monochromator. The light intensity was measured by means of a thermopile (Kipp and Zonen CA 1) or an actinometer by the use of potassium ferric oxalate. The intensity was changed by the use of neutral filters. The following data were taken using cells left for more than a few hours in the dark with an applied DC voltage.

Results

Shape of the Photoresponse Curve. In the pattern of photoresponse, the time required to reach the steady-state was between a second and a few minutes for the fresh films in a high vacuum. For the samples exposed in the air and also for the pre-treated ones, the response time was a little longer than that of the fresh film.

The decay curve of the photocurrent after the light had been turned off did not obey either the first- or second-order decay, and it showed a long tail, especially in the case of pre-treated films.

Voltage-dependence. The dark current of the fresh film left in the dark for a long time was too small to be observed at room temperature in a high vacuum. Its surface specific resistivity (ρ_{20}) was larger than $10^{19}\Omega$. On the other hand, the dark current of the pre-treated film was large enough to be measured (for instance, $\rho_{20}=1\times10^{18}\,\Omega$ for a UV-light-irradiated film in a high vacuum) and obeyed Ohm's law.

The photocurrents of both films obeyed also Ohm's law regardless of the wavelength of the illuminating light and the ambient gas.

Light-intensity Dependence. Figure 1 shows the light-intensity dependence of the photocurrent. The α value in the equation $i_{\rm ph}\propto L^{\alpha}$, where L is the light intensity, was 1.0 in a high vacuum and 0.6—0.8 in the air for the fresh film. On the other hand, for the pre-treated films the α values were 0.6—0.9 both in a high vacuum and in the air. The lowering of the α value may be due to the introduction of some shallow trap levels by air or by pre-treatment, as has been reported in the case of polyethylene film by Yahagi *et al.*[17]

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[1] K. Okamoto, Y. Hasegawa, S. Kusabayashi, and H. Mikawa, This Bulletin, **41**, 2563 (1968).

[2] Y. Hayashi, M. Kuroda, T. Imura, and A. Inami, *Kobunshi Kagaku*, **21**, 557 (1964).

[3] M. Lardon, E. L. Doller, and J. W. Weigl, *Mol. Crystals*, **2**, 241 (1967).

[4] P. J. Regensburger, *Photochem. Photobiol.*, **8**, 429 (1968).

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

[6] D. M. Pai, *ibid.*, **52**, 2285 (1970).

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

[8] H. Bauser and W. Klöpffer, *Chem. Phys. Lett.*, **7**, 137 (1970).

[9] R. C. Hughes, *ibid.*, **8**, 403 (1971).

[10] H. Inoue, K. Noda, S. Takiuchi, and E. Imoto, *Kogyo Kagaku Zasshi*, **65**, 146 (1962).

[11] K. Morimoto, E. Ishida, and A. Inami, *J. Poly. Sci. A*-1, **5**, 1699 (1967).

[12] K. Tanikawa, T. Ishizuka, K. Suzuki, S. Kusabayashi, and H. Mikawa, This Bulletin, **41**, 2719 (1968).

[13] S. Yoshimoto, K. Okamoto, H. Hirata, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 358 (1973).

[14] S. Moriwaki, K. Okamoto, S. Kusabayashi, and H. Mikawa, to be published in this Bulletin.

[15] K. Morimoto, Y. Murakami, and M. Ikeda, *National Technical Reports*, (Kadoma), **15**, 125 (1969) (in Japanese).

[16] Y. Maruyama and H. Inokuchi, This Bulletin, **39**, 1418 (1966).

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

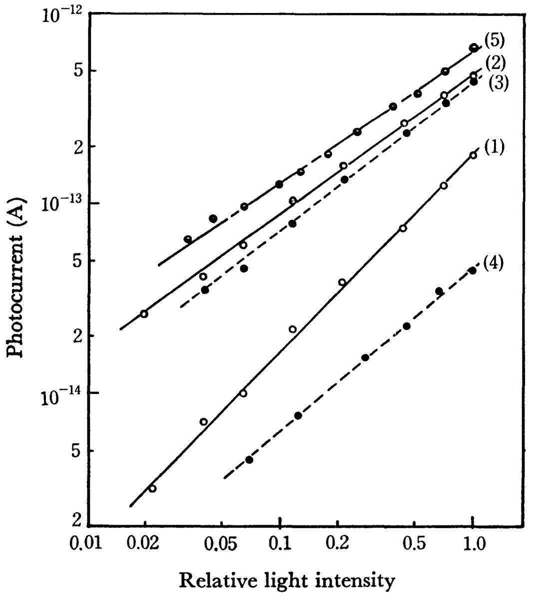

Fig. 1. Light intensity dependence of the photocurrent in a PVCz surface-type cell.
360 mμ (or 500 mμ) light at 24 °C under 3000 V/cm.
(1) a fresh film in high vacuum, (2) a fresh film in the air, (3) a film irradiated with γ-ray in high vacuum, (4) a film irradiated with γ-ray in high vacuum (500 mμ illumination), and (5) hot-pressed film in the air.

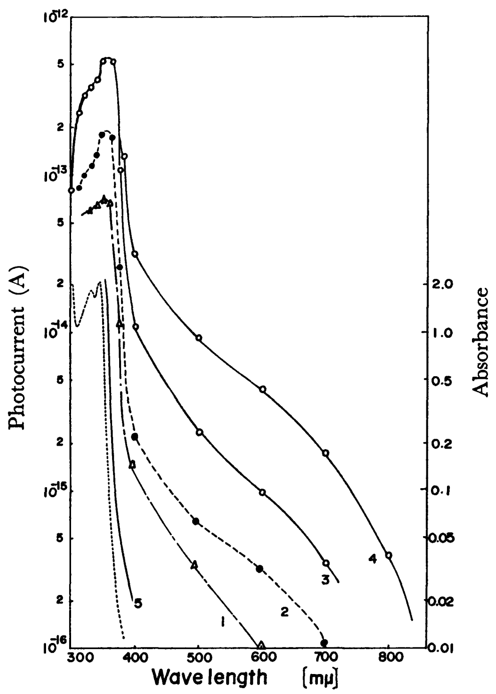

Fig. 2. Spectral dependence of the photocurrent of the fresh film in a surface-type cell for the light of 2×10^{13} photons/cm^2 s under 3000 V/cm at 23 °C.
(1) first run in high vacuum, (2) after heat treatment at 120 °C for 10 hr in high vacuum, (3) first run in the air, (4) after standing for a long time in the air, (5) absorption spectrum of the film 15 μ thick (The absorption spectrum of a film 3 μ thick is also given by a dotted line order to show the π-π* absorption band).

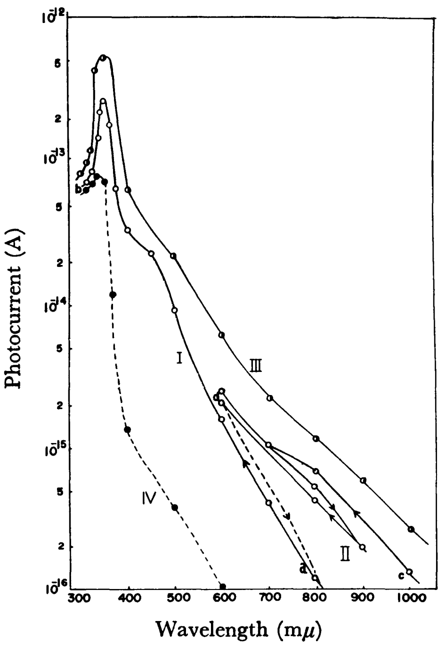

Fig. 3. Spectral dependence of the photocurrent in surface-type cells of the pre-treated films for the light of 2×10^{13} photons/cm^2 s. Effect of the repeated illumination of near-IR light was investigated. 3000 V/cm in high vacuum at 20 °C.
(I) The photocurrent of a UV-light irradiated film was measured from the wavelength (a) to (b). (II) Immediately after (b), the photocurrent was measured in the near-IR region from (c) to (d). This shows that the repeated illumination with near-IR light lowers the photocurrent progressively to the curve (I). (III) a film irradiated with γ-ray (2×10^6R). (IV) Fresh film, for comparison.

Spectral Response. Figures 2 and 3 show the spectral responses of the photocurrent for various films, the current being normalized for the relative light intensity according to the results shown in Fig. 1.

Fresh films have the photocurrent peak at 350—360 mμ and the threshold at 600 mμ. The wavelength for the minimum detectable photocurrent, 10^{-16} A, was taken as a threshold. After the film had been heated for a long time in a high vacuum (120 °C, 10 hr) or illuminated many times with UV light in a high vacuum, the photocurrent became larger in the UV as well as in the visible region and the threshold shifted to a longer wavelength region. The introduction of air had the same effect. As is shown by Curve (4) in Fig. 2, the photocurrent became larger in the air and the threshold shifted to 900 mμ. This effect of air was reversible so long as the cell was not exposed to UV illumination for a long time in the air.

In the case of the pre-treated films, the photocurrent was larger than that of the fresh film in all the wavelength regions, especially in the visible and near-IR regions, and showed the threshold at 1000 mμ even in a high vacuum, as is shown in Fig. 3. This large photocurrent in the visible and near-IR regions became still larger with pre-illumination by UV light and gradually became smaller with repeated illuminations by visible or near-IR light, as is shown in Fig. 3. Films with large photocurrents in the visible and near-IR regions showed quite large dark currents compared with that of the fresh film. Thus, there was a resemblance in the effect of the pre-treatments on the photocurrent in the visible or near-IR regions and on the dark

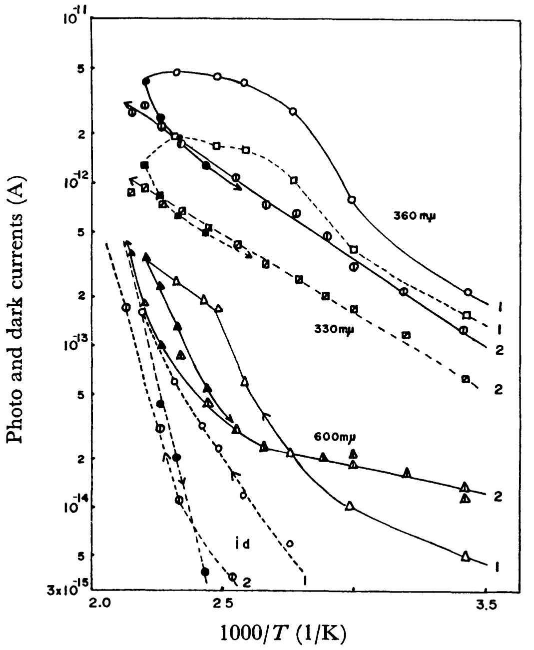

Fig. 4. Temperature dependence of the dark and photo current in a PVCz surface-type cell.
A fresh film under 3000 V/cm in high vacuum. 1 and 2; first and second heating runs, respectively.

current.

Temperature-dependence and Activation Energies.

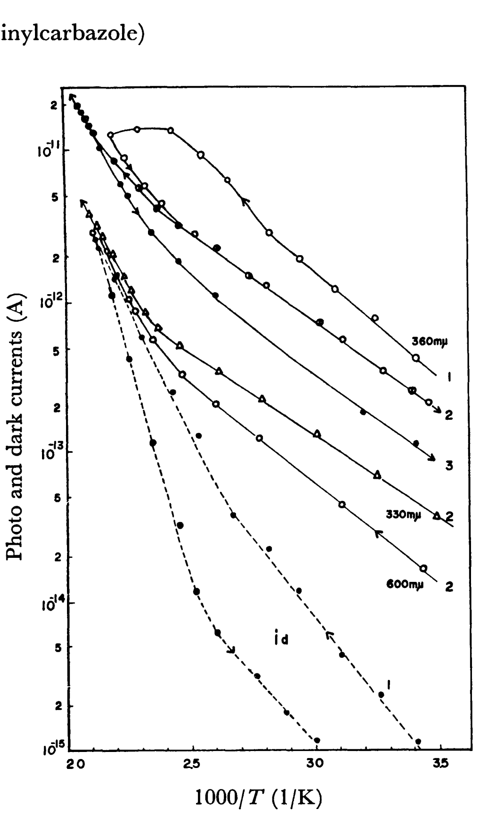

Fig. 5. Temperature dependence of the dark and photo currents in a PVCz surface-type cell.
A film irradiated with γ-ray (1×10^6R) under 3000 V/cm in high vacuum. 1, 2, and 3; first, second and third heating runs, respectively.

Figures 4 and 5 show the temperature dependence of the photo and dark currents for the fresh film as well as for the pre-treated films. In these figures, the photocurrent in the first heating run increases steeply at first, reaches the saturation point, and finally even decreases in some cases. This initial increases must be due to some unknown heat effect, while the subsequent saturation or decrease (at higher temperatures, above 120 °C) must be due to the desorption of oxygen. It has been reported that, in molecular crystals, the complete elimination of the adsorbed oxygen molecules was possible only by sublimation in a high vacuum.[16] The temperature dependence of dark and photo currents observed after two or three heating cycles was inferred to be free from the above-mentioned heat effect and oxygen desorption effect. The values of activation energies (ΔE_d and ΔE_{ph}) shown in Table 1 were thus obtained.

Discussion

Effects of Air, Hot-press, and Irradiation with UV light or γ-Rays. It is well known that the ambient gas exerts significant effects on the electrical conduction

TABLE 1. ACTIVATION ENERGIES FOR DARK AND PHOTO CONDUCTIVITIES (ΔE_d AND ΔE_{ph}) IN A PVCz SURFACE-TYPE CELL[a)]

Sample	ΔE (eV)					
	ΔE_d		ΔE_{ph} (Visible light illumination)		ΔE_{ph} (UV light illumination)	
	low	high	low	high	low	high
Fresh film[c)]	(b)	1.0—1.3 (120—200 °C)	0.06—0.20 (20—120 °C)	0.7—1.0 (~200 °C)	0.16—0.22 (20—120 °C)	0.16—0.22 (~200 °C)
Fresh film[d)]	0.7—0.8 (50—120 °C)	—	0.3—0.6 (20—120 °C)	—	0.5—0.6 (20—120 °C)	—
Film irradiated with UV light[c)]	0.47 (50—100 °C)	0.80 (80—200 °C)	0.20 (20—100 °C)	0.70 (~200 °C)	0.23 (20—130 °C)	0.68 (~200 °C)
Film irradiated with γ-rays[c)]	0.4—0.5 (40—110 °C)	0.8—1.0 (~200 °C)	0.24 (20—130 °C)	0.40 (~200 °C)	0.23 (20—140 °C)	0.40 (~200 °C)

a) Activation energy (ΔE) is represented by the equation $i \propto \exp(-\Delta E/kT)$.
b) Only on the first heating, a fresh film showed a small dark current similar to the thermally stimulated current at this low temperature range. Thereafter, the current was too small to be measured.
c) In high vacuum under 3000 V/cm.
d) In air under 3000 V/cm.

in a surface-type cell.[18] The following effects of air on the electrical conduction were observed in a PVCz film: (a) an increase in the dark current with a lowering of ΔE_d; (b) an increase in the photocurrent in all the wavelength regions and a red shift of the threshold of the photocurrent; (c) a lowering of the α value of the light-intensity dependence of the photocurrent; (d) an increase in ΔE_{ph}, and (e) an increase in the rise time of the photocurrent and a long tail in the decay curve of the photocurrent.

The oxygen molecule acts as an electron acceptor because of its large electron affinity, and the resulting O_2^- molecule may act as a hole-trapping center.[19] These effects of air may be explained by supposing that, in the air, impurity levels acting as shallow hole-trapping centers are introduced into a PVCz film by oxygen molecules.

Such pre-treatments in the air as hot-press and irradiation by UV light or γ-rays had effects on the photocurrent similar to the effects of air. Any electron-accepting or hole-trapping levels may be introduced by these pre-treatments.

Origin of Both the Dark Current and the Photocurrent in the Visible and Near-IR Regions. The resemblance in the effects of the pre-treatments on the photocurrent in the visible and near-IR regions and on the dark current suggest that, in both cases, the carriers are generated from the same origins, which are increased by air, hot-press, or irradiation with UV light or γ-rays. In every film the value of ΔE_d was less than 1.3 eV. As this value is much smaller than the estimated band gap energy ($\sim$4.4 eV[20]), the intrinsic carrier generation must be ruled out. Other possible carrier generation process in the dark are (1) carrier injection from the electrode and (2) the ionization of acceptors or donors, which can release carriers by means of the thermal process.

The possibility of the carrier injection from the electrode can be ruled out on the basis of the following findings: (a) the dark current did not obey the Schottky equation, but Ohm's law[21]; (b) the electrode materials (Au, Ag, Cu, and Al) had no effect on the dark and photo currents,[21] and (c) the magnitude of the dark and photo currents was strongly influenced by UV pre-illumination or by repeated near-IR illuminations.

In a PVCz surface-type cell the dark current and the photocurrent may, therefore, be mainly due to the thermal or optical reexcitation of trapped carriers. In the pre-treated films, trapped carriers will increase with an increase in the number of trap centers introduced by the pre-treatments, thus resulting in an enhanced dark current and photocurrent in the visible and near-IR regions.

Activation Energy for Dark and Photo Conductions. As is evident from Table 1, the values of ΔE_d and ΔE_{ph} change considerably both with the temperature and with the wavelength of illuminated light. Except in the case of ΔE_{ph} for UV illumination in a fresh film, in every film the values of ΔE_d and ΔE_{ph} in the high temperature range are considerably larger than the values in low temperature range; the former values are also large as compared with those in the case of such aromatic hydrocarbons as anthracene. A similar phenomenon has been reported for polyethylene[23] and for the polymers prepared by glow-discharged polymerization.[24] In polyethylene Tanaka *et al.* have explained this phenomenon in terms of a "trapping conduction mechanism".[23] As has been mentioned above, both the dark current and the photocurrent in the visible and near-IR regions are due to the reexcitation of trapped carriers. The process of the reexcitation by light must not need a large activation energy. The large values of ΔE_{ph} in the high temperature range, therefore, suggest that these activation energies are needed mainly for carrier migration. A trapping conduction mechanism similar to the case of polyethylene is applicable to the photo- and dark-conductions in a PVCz surface-type cell as follows.

The exact profile of trap distribution is not yet available. However, if one considers a "hypothetical trap" which is defined as a discrete level corresponding to a special distribution of trapped carriers under conditions leading to a measured ΔE_d or ΔE_{ph}, then one can draw an energy diagram such as is shown in Fig. 6. In this diagram, a deep trap (E_{t4}) is also shown, though it has not been dicussed in this paper.

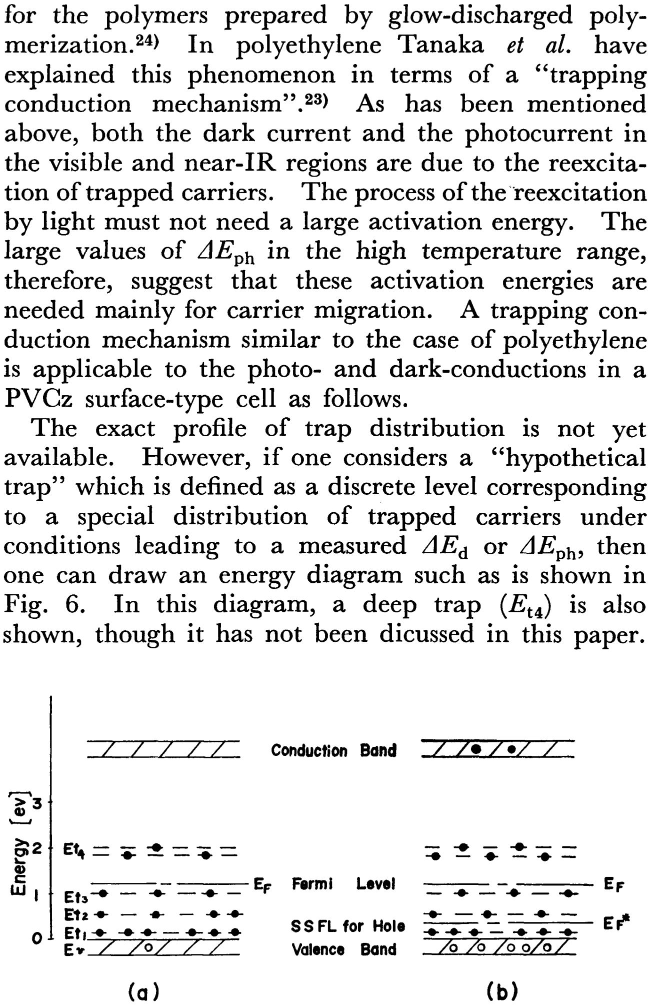

Fig. 6. Energy level model for a PVCz fresh film in high vacuum. As concerns the levels ($E_{t1}\sim E_{t4}$), see text.
(a) in the dark in low temperature range. (b) under UV or visible illumination in low temperature range.

Supposing that the Fermi level (E_F) exists between E_{t2} and E_{t3} or a little higher than E_{t3} below 120 °C, as the reexcitation of holes from the energy states much higher than E_F (E_{t3} or E_{t4} in the present case) is negligible, the energy states a little lower than E_F (E_{t2} or E_{t3} in the present case) will play an important role in

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18) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, Inc., New York, (1967), p. 197.

19) H. Kokado and W. G. Schneider, *J. Chem. Phys.*, **40**, 2937 (1964). A. Bree and R. A. Kydd, *ibid.*, **40**, 1775 (1964).

20) W. Klöpffer, *Z. Naturforsch.*, **24a**, 1923 (1969).

21) As will be reported in the succeeding paper of this series,[22] sandwichtype cells were examined over a wide range of field strengths up to 330000 V/cm with several kinds of electrode materials. The information thereby obtained also suggests the impossibility of electrode injection.

22) K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 1953 (1973).

23) T. Tanaka and T. Inuishi, *Jap. J. Appl. Phys.*, **6**, 1371 (1967).

24) T. Hirai and O. Nakada, *Reports on Progress in Polymer Physics in Japan*, **VIII**, 333 (1965). A. Bradley, *Trans. Faraday Soc.*, **61**, 773 (1965).

trapping hole carriers. The ΔE_d value in this temperature range, which could not be measured in the present study, may thus be estimated to be E_{t2} or E_{t3}, that is, 0.7—1.0 eV or 1.0—1.3 eV. With UV illumination, some holes and electrons are created by the extrinsic mechanism[25] and the distribution of holes in the dark (Fig. 6(a)) changes, thus resulting in Fig. 6(b). The increasing concentration of holes in the valence band leads to a lowering of the Fermi level to the steady-state Fermi level for hole ($E_F{}^*$), and the trap level below $E_F{}^*$ acts as a shallow trap and the level above $E_F{}^*$ as a deep trap.[26] Now, supposing that $E_F{}^*$ exists between E_{t1} and E_{t2}, the trap levels associated with E_{t2} must be filled with holes and the levels associated with E_{t1} must act as effective trapping centers for migrating holes. Therefore, the ΔE_{ph} value under UV illumination is 0.1—0.2 eV ($=E_{t1}$) in the low-temperature range.

In the case of visible illumination in the low-temperature range, the photocurrent is much larger than the dark current. Therefore, the steady-state Fermi level must be lowered so far as below E_{t2} according to the increase in the current under visible illumination. The trap levels associated with E_{t1} act as effective trapping centers for migrating holes, and the ΔE_{ph} value under visible illumination is 0.1—0.2 eV in the low-temperature range. Above 120 °C the Fermi level probably rises to much above E_{t3}. In the dark the trap levels associated with E_{t3} act as effective trapping centers and the ΔE_t value is 1.0—1.3 eV.

Under UV illumination the steady-state Fermi level is probably lowered so far as below E_{t2} according to the number of holes created, in the same manner as in the case of the low-temperature range, and the ΔE_{ph} value is 0.1—0.2 eV even at high temperatures. In the case of visible or near-IR illumination, the photocurrent is not so large as the dark current in the high-temperature range and the steady-state Fermi level for hole is lowered to near E_{t3} or E_{t2} at most. The ΔE_{ph} value in this case becomes 0.7—1.0 or 1.0—1.3 eV.

A similar explanation is possible for the conductions in the pre-treated films.

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

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