Photoconductivity of Vinyl Polymers with Large Pendant π-Electron Systems. I. Poly-9-vinylacridine

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The dark- and photo-conductivities of poly-9-vinylacridine (PVAcr) were investigated in comparison with those of poly-*N*-vinylcarbazole (PVCz). The dark current was ohmic over the whole voltage region studied up to 150000 V/cm. The photocurrent showed a linear dependence on the applied voltage even in fairly high applied fields up to 130000 V/cm and a spectral dependence corresponding antibatically to the absorption spectrum. The magnitude of the photocurrent with positive electrode illumination (i^+_{ph}) was only 1.5—2 times larger than that with negative electrode illumination (i^-_{ph}), the behavior differing entirely from that in a PVCz film. The magnitude of the photocurrent of PVAcr was smaller than that of PVCz by several times for i^-_{ph} and by a hundred times for i^+_{ph}. The poor photoconductivity of PVAcr was attributed both to the high concentration of the excimer-forming site acting as an effective exciton trap and to the poor electron-donating character.

The electrical conductivity of vinylpolymers with pendant π-electron systems has been extensively investigated.[1-10] Most investigations have been done with poly-*N*-vinylcarbazole (PVCz), being used as the material for electrophotography. The large photoconductivity of PVCz is attributed both to the good efficiency of the carrier generation through the field-assisted thermal dissociation of an exciplex formed between an excited carbazolyl group and some electron-accepting impurity, and to the ease of the carrier migration through the overlap of π-orbitals of neighboring carbazolyl groups in one polymer chain.[10] In other words, it is due to the presence of the short-range electronic interaction (such as the electron exchange interaction) between neighboring carbazolyl groups in one polymer chain, which are bulky and have a fairly low ionization potential. This has been confirmed by the fact that the photoconductivity of PVCz is much superior to that of poly-*N*-carbazolylethylvinylether where carbazolyl groups are connected far apart from the skeletal chain and the short-range electronic interaction between neighboring carbazolyl groups is very weak.[11]

On the basis of investigation on both the UV spectra of a series of the vinylpolymers[12] and their NMR spectra,[13] it has been found that the vinylpolymers with large pendant π-electron systems such as poly-9-vinylacridine (PVAcr) and poly-1-vinylpyrene have also some electronic interactions between neighboring pendant chromophores in one polymer chain even in solution in a manner similar to the case of PVCz. It is, therefore, very important to investigate the photoconductivity of these polymers in comparison with that of PVCz in order to obtain information on the factors determining the photoconductivity of the vinylpolymers. This paper deals with the steady-state photoconductivity of PVAcr in a sandwich-type cell.

Experimental

PVAcr was prepared by anionic polymerization of the monomer with Na-naphthalene complex at room temperature,[14] and reprecipitated three times from chloroform (containing 1% ethanol) solution with *n*-hexane. The average molecular weight of the polymer thus prepared was determined to be 20000 with use of a membrane osmometer.

Thin films (15 or 9 μm thick) of the polymer undoped and doped with 0.5 mol% of *p*-chloranil (CA) were made on nesa-coated quartz plates from the chloroform solution. Semitransparent gold main and guard electrodes were evaporated on the film to prepare a sandwich-type cell. The cell was used for the electrical conductivity measurements without exposure to the air after the evaporation of the metal electrodes. Measurements were carried out by the DC method in a vacuum ($10^{-7}-10^{-8}$ Torr) or in the air. A 500 W xenon lamp monochromatized by a grating monochromator was used as a light source.[10]

Results and Discussion

Dark Conductivity. PVAcr showed an ohmic dark current (specific conductivity at 60 °C, $\sigma_{60}=3\times10^{-19}\,\Omega^{-1}\,\text{cm}^{-1}$ in a high vacuum) over the whole voltage region up to 150000 V/cm. The activation energy of the dark current was 1.0 eV. The behavior differs from that in PVCz films which show a nonohmic dark current attributable to either Poole-Frenkel[2] or Richardson-Schottkey effects.[1] With doping of CA, the dark current increased by several times but the activation energy hardly varied at all.

Photoconductivity. The photocurrent showed two types of response curves (Fig. 1). Illumination with the weakly-absorbed light ($\lambda>400$ nm) induced a photocurrent of Type A, while the illumination with the strongly-absorbed light ($\lambda\leq400$ nm) induced that of Type B. The photoresponse curve of Type B seems to be attributable to the effect of space charges built up by the illumination with the strongly-absorbed light.[15] The results were obtained for the steady-state value of the photocurrent.

The voltage dependence of the photocurrent is shown in Fig. 2. The photocurrents in the films, undoped and doped with CA, were proportional to the applied voltage in the fields lower than 70000 V/cm. The superlinear dependence of photocurrent on the applied voltage, regarded as an important character of the photoconductivity of PVCz,[10] was exceptionally observed for the photocurrent induced with the light

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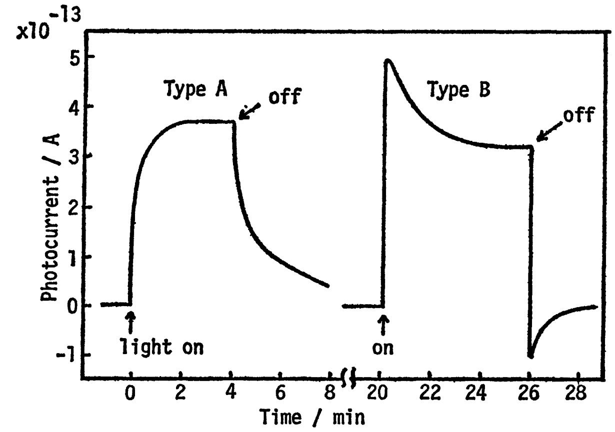

Fig. 1. Representative photoresponse curves in a PVAcr sandwich-type cell.

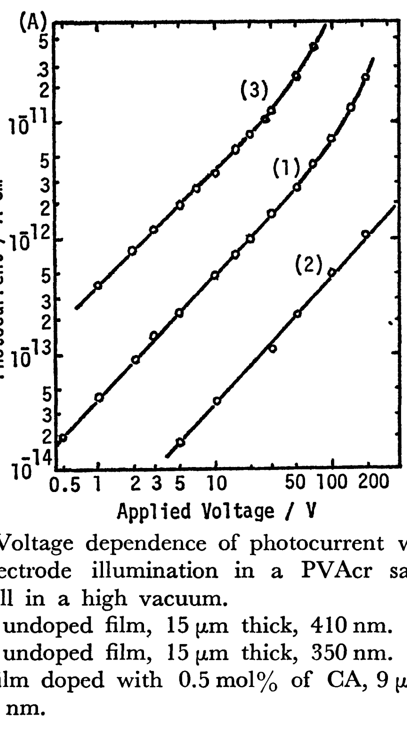

Fig. 2. Voltage dependence of photocurrent with positive electrode illumination in a PVAcr sandwich-type cell in a high vacuum.

(1) an undoped film, 15 μm thick, 410 nm.

(2) an undoped film, 15 μm thick, 350 nm.

(3) a film doped with 0.5 mol% of CA, 9 μm thick, 410 nm.

of 410 nm in fields higher than 70000 V/cm. The voltage at which the superlinearity appeared was larger for PVAcr than for PVCz by 10 times.

The photocurrent was always proportional to the light intensity (10^{12}—10^{14} photon/cm^2 s) regardless of doping of CA.

Plots of logarithm of the photocurrent *vs.* $1/T$ gave a straight line over the whole temperature range (20—130 °C). The activation energy of the photocurrent was 0.18±0.03 eV at 360—410 nm under 35000V/cm and varied little with doping of CA. The value is nearly equal to that for PVCz.

The spectral dependence of the photocurrent is shown in Fig. 3. It was obtained by normalizing the observed photocurrent values to a constant light intensity, 2×10^{13} photon/cm^2 s. It was not affected by the polarity of the illuminated electrode, applied voltage, ambient oxygen and doping of CA. The photocurrent peaks appeared at 410 and 290 nm corresponding to the wavelength of the absorption edge of the ^1L_a band and the absorption minimum between the ^1L_a and ^1B_a bands, respectively. The photocurrent minimum appeared at 360 nm corresponding to the wavelength of the absorption maximum of the ^1L_a band. The spectral dependence, thus, corresponded antibatically to the absorption spectrum.

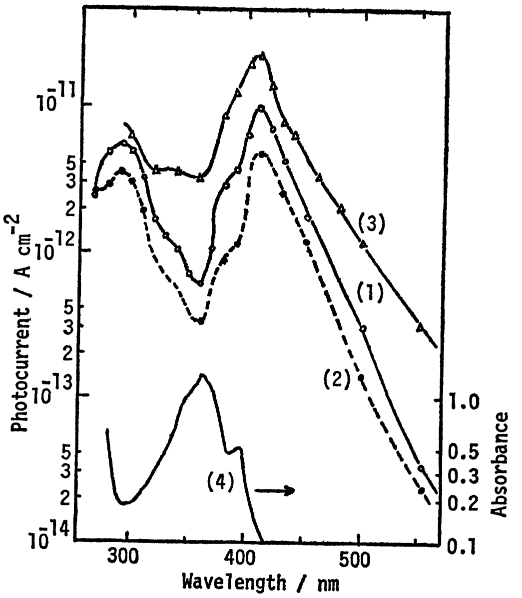

Fig. 3. Spectral dependence of photocurrent with positive electrode illumination in a PVAcr sandwich-type cell under an applied field of 33000 V/cm at a light intensity of 2×10^{13} photon/cm^2 s.

(1) an undoped film, 15 μm thick, in a high vacuum.

(2) an undoped film, 15 μm thick, in the air.

(3) a film doped with 0.5 mol% of CA, 9 μm thick, in a high vacuum.

(4) absorption spectrum of an undoped film (0.5 μm thick).

In general, for a film thick enough to absorb the light almost completely, the type of spectral dependence mentioned above appears when the carrier generation in the bulk is predominant, while the other type of spectral dependence of the photocurrent corresponding symbatically to the absorption spectrum appears when the surface carrier generation is predominant. In a PVAcr film, the latter type was not observed even under 70000 V/cm, and the photocurrent with positive electrode illumination (i_{ph}^{+}) was larger than that with negative electrode illumination (i_{ph}^{-}) only by 1.5—2 times in magnitude. These results are quite different from those for PVCz; in a PVCz film under an applied field higher than 7000 V/cm, i_{ph}^{+} showed the latter type of spectral dependence, being much larger than i_{ph}^{-} in magnitude (*e.g.*, 20—100 times at 35000 V/cm).[10] From Fig. 4 which shows a comparison of the photocurrents observed for PVAcr and PVCz films under the same experimental condition, we see that the magnitude of the photocurrent of PVCz is larger than that of PVAcr by several times for i_{ph}^{-} and by a hundred times for i_{ph}^{+}. Judging from these results and the absence of the superlinearity of the photocurrent on applied voltage in a PVAcr film, the surface carrier generation does not seem to be predominant in

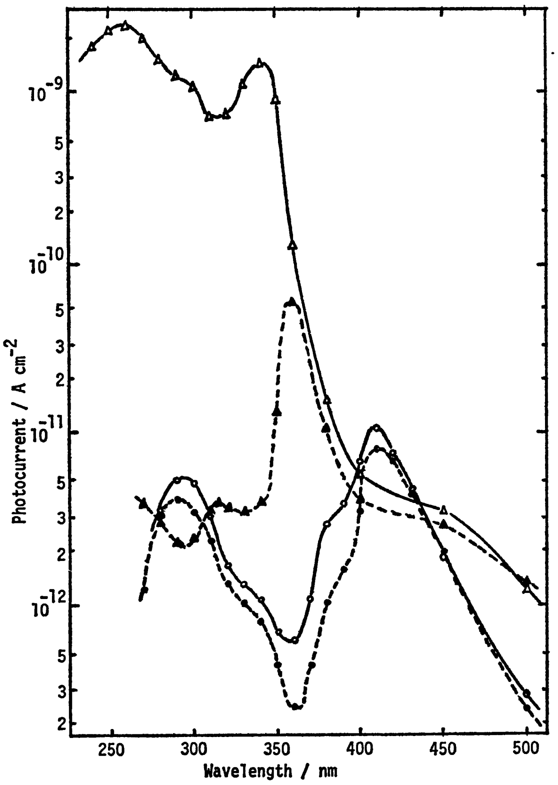

Fig. 4. A comparison of the magnitudes of the photocurrents between PVAcr and PVCz.
The photocurrents were measured in sandwich-type cells (15 μm thick) under an applied field of 33000 V/cm at 2×10^{13} photon/s in a high vacuum of 10^{-7} Torr at 20 °C.
(—○—): PVAcr, positive electrode illumination,
(--●--): PVAcr, negative electrode illumination,
(—△—): PVCz, positive electrode illumination,
(--▲--): PVCz, negative electrode illumination.

a PVAcr film even under a fairly high applied field (130000 V/cm), although it has been considered to be a predominant carrier generation process in a PVCz film.

With doping of CA, the photocurrent increased over the whole wavelength region by 2—3 times with no distinct change in the spectral dependence. No new photocurrent peak was found in the charge-transfer absorption region. This is not surprising, since the charge-transfer absorption band ($\lambda_{\max}=535$ nm in $CHCl_3$ solution) could hardly be found in the film (9 μm thick) doped with 0.5 mol% of CA. A film doped heavily with CA could not be used for the electrical measurements, since it easily cracked.

Although PVAcr is not considered to be inferior to PVCz as regards the electronic interaction between neighboring pendant groups in one polymer chain on the basis of their UV and NMR spectra,[12)] the photoconductivity of PVAcr is greatly inferior to that of PVCz. In a PVCz film, the surface carrier generation through an exciplex formed between a singlet exciton and some electron-accepting impurity has been considered to be predominant even under a fairly low applied field. In a PVAcr film, however, such a surface carrier generation does not seem to be predominant even under a fairly high applied field. This is a reason for the poor photoconductivity of PVAcr.

A singlet exciton migrates efficiently in a polymer film and the migration is strongly affected by the inherent trapping site such as the excimer-forming site.[16)] PVAcr shows exclusively excimer fluorescence not only in solid but also in a solution with no monomeric fluorescence.[17)] This is probably due to the high concentration of the excimer-forming site. In this case, a singlet exciton is considered to cover only a small number of acridine rings during its life time, because its migration is limited by the excimer-forming site. As one of the most conceivable carrier generation process in an undoped PVAcr film, we can assume the field-assisted thermal dissociation of an exciplex ($(D^{\delta+}\cdots A^{\delta-})^*$) formed between a singlet exciton (D^*) and some electron-accepting impurity (A) to the ion radicals (D^+ and A^-), as is the case with PVCz[10)]

$$D^* + A \longrightarrow (D^{\delta+}\cdots A^{\delta-})^* \longrightarrow D^+ + A^- \qquad (1)$$

However, the efficiency of this carrier generation might be poor for a PVAcr film because of the limitation of the exciton migration. The situation is the same as for the other extrinsic carrier generation mechanisms such as the interaction between the electrode and a singlet (or triplet) exciton. The high concentration of the excimer-forming site, therefore, may be the main cause for the poor photoconductivity of PVAcr.

In general, the efficiency of extrinsic or intrinsic photo-carrier generation increases with an increase in the electron-donating character of the aromatic rings. The situation is the same as for the carrier generation due to the dissociation of an exciplex (Eq. 1), because of an increase in the degree of charge-transfer in the exciplex state, $(D^{\delta+}\cdots A^{\delta-})^*$, with the electron-donating character. Another reason for the poor photoconductivity of PVAcr may be the poor electron-donating character of PVAcr; the first ionization potential has been determined to be 7.88 eV for PVAcr and 7.43 eV for PVCz, from the energy of the first charge-transfer absorption in chloroform solution.[18)]

From the viewpoint of intensity of the electronic interaction between neighboring pendant chromophores in one polymer chain examined by the UV, CT, and NMR spectra,[12,13,18)] the carrier mignation may be assumed to be as easy in a PVAcr film as in a PVCz film. The poor photoconductivity of PVAcr is, therefore, attributable mainly to the poor efficiency of carrier generation, although it remains ambiguous whether the excimer-forming site acts as an effective carrier trapping site.

The discussion mentioned above reconfirmed that the good photoconductivity of PVCz is due to both the comparatively low ionization potential of the carbazolyl groups and the low concentration of the excimer-forming sites in the polymer, in spite of the presence of the short-range electronic interactions between neighboring pendant carbazolyl groups.

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