

# Photovoltaic Properties of the Poly-2-vinylpyridine Iodine Complex—SnO<sub>2</sub> System

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## Synopsis

Amorphous films of poly-2-vinylpyridine—I<sub>2</sub> complex have strong absorption over the entire visible spectrum. The photovoltaic properties of solar cells made from thick films of the polymer-iodine complex deposited over a tin oxide layer have been studied. The conversion efficiency of white light into electricity is  $5 \times 10^{-2}\%$ . This transformation yield is obtained by combining a low open-circuit voltage with a rather high short-circuit current.

## INTRODUCTION

Our laboratory is presently engaged in the search for new photovoltaic organic materials which can be used for direct conversion of light power into electrical power. Our attention was drawn to poly-2-vinylpyridine doped with iodine for two reasons: (a) Complexes of polyvinylpyridines and I<sub>2</sub> with resistivities as low as  $10^4 \Omega\text{-cm}$  have been described<sup>1</sup>; (b) the increase of conductivity of polymer—I<sub>2</sub> complexes such as poly(vinylcarbazole)—I<sub>2</sub> when subjected to irradiation with visible light is well documented.<sup>2,3</sup>

We report in this paper some properties of a tin oxide |poly-2-vinylpyridine—I<sub>2</sub>| platinum cell.

## EXPERIMENTAL

Poly-2-vinylpyridine (PVP) of two different origins was used for the preliminary experiments. These were (i) commercial PVP (Aldrich) purified by solubilization in benzene followed by precipitation with hexane and (ii) PVP polymer synthesized by initiation with benzoyl peroxide under the conditions used by Lupinsky et al.<sup>4</sup> The commercial PVP gave consistently higher electrical resistivity after treatment with I<sub>2</sub> vapor; thus the results reported in this paper are those obtained with the PVP synthesized in our laboratory. A molecular weight of  $9.04 \times 10^4$  was estimated by viscosimetry.

The samples were prepared in the form of 10–50- $\mu\text{m}$  layers obtained by slow precipitation of poly-2-vinylpyridine from chloroform (30 mg/mL) at room temperature. The support material, *n*-tin oxide deposited on glass, is supplied by PPG Industries (Nesa glass  $100\Omega_{\square}$ ). The complex PVP—I<sub>2</sub> is formed by interaction of the solid polymer with iodine vapor at 100°C. The amount of I<sub>2</sub> introduced is conveniently monitored by weighing the samples. X-ray diffrac-

tion patterns show that the PVP films are essentially noncrystalline; the amorphous character is further increased by complexing with  $I_2$ .

A typical configuration of the cells is shown in Figure 1.

To improve the contact between the Pt foil and the polymer, the samples were heated at  $100^\circ\text{C}$  with clips between the back and front contacts.

The electrical measurements were performed at room temperature. The electrical conductivity of the cells was obtained using a Heathkit IP-2071 power supply; the voltages were measured with a Keithley 616 Digital electrometer and the currents with a Solartron 7051 DVM. The dark characteristics between  $-0.6$  and  $+0.6$  V were independent of time; at higher voltages, a slow decrease of the current as a function of time was observed. The photocurrent in the time range of a few seconds to several hours was quite stable. No modification of the electrical properties was observed during irradiation.

The white light source was a Xenon 150-W illuminator powered by a Varian PS 150-8 supply. The beam was passed successively through water and 2 cm of a saturated  $\text{CuSO}_4$  solution. Nesa glass is transparent at  $\lambda < 350$  nm. Under typical conditions, the beam power measured with a calibrated Si solar cell was  $2 \text{ mW}\cdot\text{cm}^{-2}$ . A Unicam SP500 monochromator was used for the experiments with monochromatic light. Unless otherwise stated, the irradiations were always performed through the transparent front contact (see Fig. 1).

## RESULTS

Before treatment with  $I_2$ , the PVP films are transparent down to 330 nm. In the presence of  $I_2$  vapor, the films become colored, and, depending on the contact time and color goes from yellow-red-brown to black. The thinnest continuous PVP films we were able to prepare were  $10 \mu\text{m}$  thick. Thinner films peeled off. Films with good conductivities have optical densities much larger than 2 in the visible region. Therefore, there are uncertainties on the exact shape of the spectra between 400 and 600 nm (dotted curve in Fig. 2). Between 300 and 1000 nm, the different species which can be responsible of light absorption are:  $I_3^-$ , the pyridine  $I_2$  charge transfer complex,  $\text{pyridine}^+ - I$ , and free  $I_2$ .<sup>5-7</sup>  $\lambda_{\text{max}}$  of these species is indicated by an arrow in Figure 2. The formation of  $I_3^-$  is observed when pyridine is mixed with  $I_2$ ; such a species would justify the uptake of almost two iodine molecules per monomeric unit.

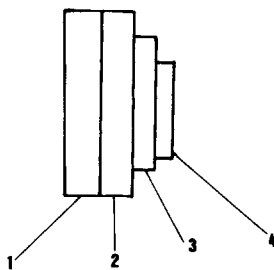


Fig. 1. Configuration of the cells.

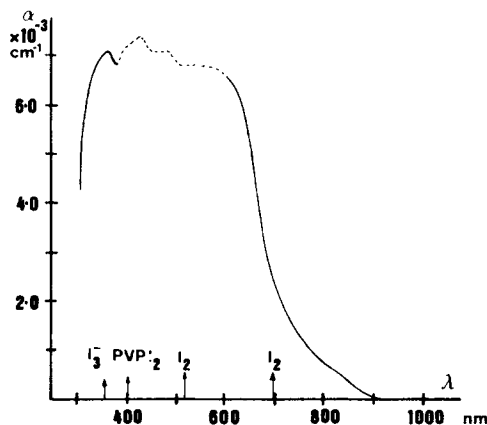


Fig. 2. UV-visible absorption spectrum of the complex.

### Current-Voltage (I—V) Characteristics

The I—V characteristic of sandwich cells SnO<sub>2</sub> |PVP—I<sub>2</sub>| Pt is strongly dependent on the iodine content of the polymer. The dynamic resistance decreases with increasing I<sub>2</sub> for any value of applied voltage. The I—V curves for three different iodine contents are given in Figure 3. Increasing the I<sub>2</sub> vapor-polymer contact times to more than 18 h (which correspond to an I<sub>2</sub>/polymer ratio of 1.8) causes no further change in the I—V characteristics. (The molar concentration of polymer is based on the repeating unit.)

The characteristics are nearly symmetrical. A weak, reproducible asymmetry is observed, however; the current is slightly larger when the SnO<sub>2</sub> contact is polarized positively. Furthermore, when the SnO<sub>2</sub> substrate is replaced by a Pt foil pressed against the polymer, the characteristic becomes ohmic, suggesting that the asymmetry is due to the SnO<sub>2</sub>-polymer contact. It was shown by the

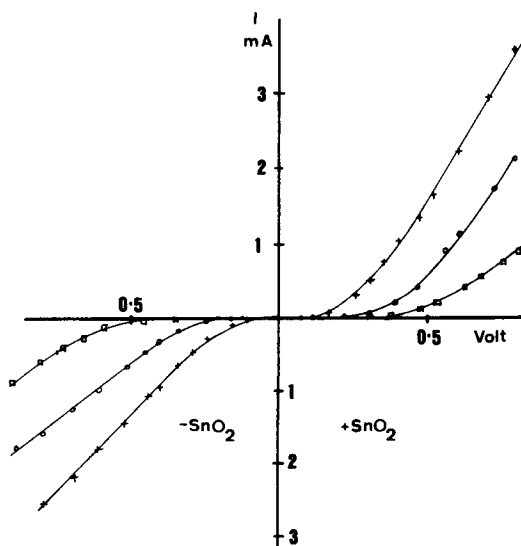


Fig. 3. I—V characteristics of SnO<sub>2</sub>|PVP—I<sub>2</sub>|Pt cells for three iodine contents: I<sub>2</sub>/polymer = 1.4; I<sub>2</sub>/polymer = 1.6; I<sub>2</sub>/polymer = 1.8.

four-point probe technique that the bulk resistance of the polymer can be neglected.

### The Pt—Polymer Contact

The I—V curve given in Figure 4 was obtained using the electrode configuration shown in the same figure. The polymer is pressed against a Pt foil and the front contact is made with a Pt wire ( $\phi = 0.02$  cm). The ratio of the areas of the two contacts is 1/10,000. The rectifying factor at 0.5 V is 50; the PVP—I<sub>2</sub>|Pt diode is forward biased when the Pt wire is negatively polarized. Changing the area ratio to 1/100, under conditions such that the polymer bulk resistivity is still negligible lead to essentially the same results.

### The SnO<sub>2</sub>—Polymer Contact

Experiments similar to those described in the previous paragraph, with either a small SnO<sub>2</sub> contact ( $\sim 2$  mm<sup>2</sup>) or a large SnO<sub>2</sub> contact ( $\sim 100$  mm<sup>2</sup>) were performed. Although there is a larger dynamic resistance, the I—V characteristics do not differ significantly from those obtained with the SnO<sub>2</sub>|PVP—I<sub>2</sub>|Pt cells (Fig. 3). It is thus confirmed that the electrical characteristic of our cell is typical of the tin oxide—(PVP—I<sub>2</sub>) interface.

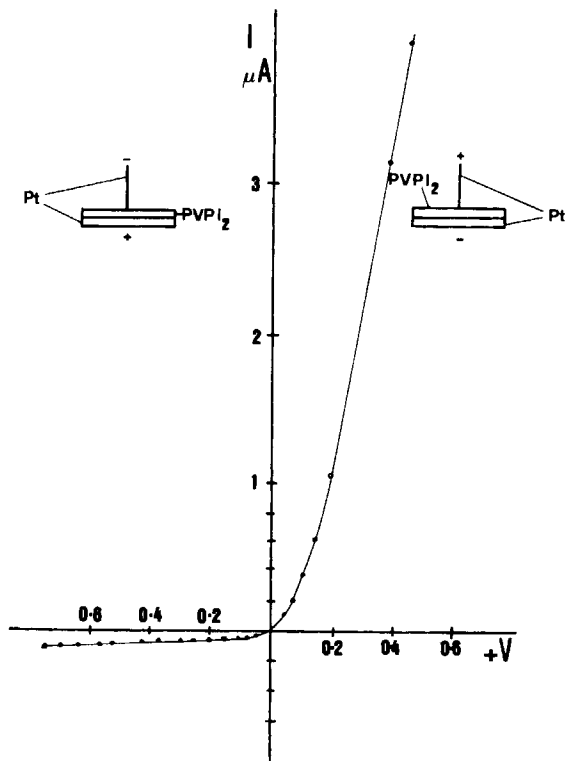


Fig. 4. I—V characteristic of the PVP—I<sub>2</sub>—Pt point contact electrode.

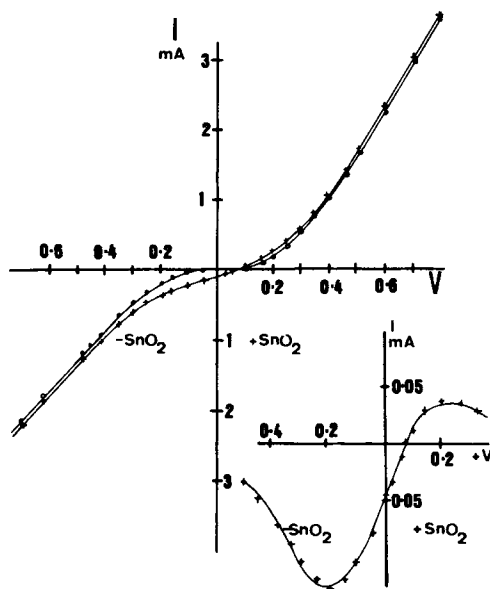


Fig. 5. (a) I—V characteristic of a SnO<sub>2</sub>|PVP—I<sub>2</sub>|Pt cell in the dark under irradiation. (b) Difference between the dark current and the photocurrent.

### Photovoltaic Effect

When the sample is subjected to white light illumination through the SnO<sub>2</sub> contact, current flows from the Pt electrode to SnO<sub>2</sub>. The I—V characteristic measured under these conditions is given in Figure 5(a); the difference between the dark current and the photocurrent is shown in Figure 5(b). The open-circuit voltage  $V_{oc}$  and the short-circuit current density  $J_{sc}$  for three I<sub>2</sub>/PVP ratios at a constant light intensity of 2 mW/cm<sup>2</sup> are given in Table I. It appears from Table I that  $V_{oc}$  decreases and  $J_{sc}$  increases with the I<sub>2</sub>/PVP ratio. This will be discussed at the end of this paper.

The characteristics of the cells are moderately reproducible; the following data were obtained with our two best cells under irradiation:

$J_{sc}$	$V_{oc}$
136 $\mu$ A	80 mV
165 $\mu$ A	73 mV

For those samples, the conversion factor of light power into electrical power is 0.05%.

TABLE I

[I <sub>2</sub> ]/[polymer]	Contact time with I <sub>2</sub> vapor at 100°C (h)	$J_{sc}^a$ ( $\mu$ A/cm <sup>2</sup> )	$V_{oc}$ (mV)
1.4	1	4.1	91.9
1.6	4	36.9	66.4
1.8	18	88.2	70.0
1.8	36	99.6	65.0

<sup>a</sup> A typical area of the sample is 1 cm<sup>2</sup>.

### Irradiation by Monochromatic Light

The short-circuit current was measured as a function of light intensity  $I_{h\nu}$  at different wavelengths between 350 and 600 nm. At longer wavelengths, the photocurrent is too small to allow a precise determination of the relation between photocurrents and  $I_{h\nu}$ . It appears that with light intensities

$$5 \times 10^{13} < I_{h\nu} \text{ (photons s}^{-1} \cdot \text{cm}^{-2}) < 5 \times 10^{15}$$

relationship (1) is obeyed and that  $\alpha$  is slightly but significantly smaller than unity:

$$I_{sc} \sim I_{h\nu}^\alpha \quad (1)$$

This is an observation typical of many organic samples, and it should be discussed in terms of cooperation of recombination and trapping centers.<sup>8</sup>

Using the following expression, the gain  $G$  was measured in the photovoltaic mode:

$$G = I_{sc}/[qI_{h\nu}A(1 - T)] \quad (2)$$

$q$  is the electron charge,  $A$  the area of the sample, and  $T$  the fraction of transmitted light. The dependence of  $G$  on the incident wavelength is shown in Table II.

The decrease of  $G$  with increasing  $\lambda$  can be assigned either to a variation of the probability of charge separation with excitation energy or to a dependence of the probability of charge separation as a function of the distance from the SnO<sub>2</sub> surface where light absorption takes place (electric-field-dependent photogeneration). The former interpretation, which is applicable to various amorphous inorganic materials such as a-Se or a-As<sub>2</sub>S<sub>3</sub><sup>9</sup> and organic polymer films,<sup>10</sup> cannot be discarded here; from the experiments described in the next subsection, however, it appears that the latter model explains the observations satisfactorily.

### Irradiation Through Front and Back Contacts

For these experiments, the back electrode is made of a Pt gauze (150 meshes/cm<sup>2</sup>). The photocurrent is given in Figure 6 as a function of the wavelength and side of illumination. Correction for the variation of the light source intensity at the different wavelengths was made. The data obtained by excitation through the SnO<sub>2</sub> contact are similar to those discussed above. The behavior of the photocurrents obtained by excitation through the Pt gauze are more interesting. The maximum photocurrent is observed at 790 nm and 750 nm for

TABLE II  
Gain Value  $G$  as a Function of Wavelength

$G$	$\lambda$ (nm)
$17 \times 10^{-2}$	380
$73 \times 10^{-3}$	400
$38 \times 10^{-3}$	450
$69 \times 10^{-4}$	510
$31 \times 10^{-4}$	550
$6 \times 10^{-4}$	600

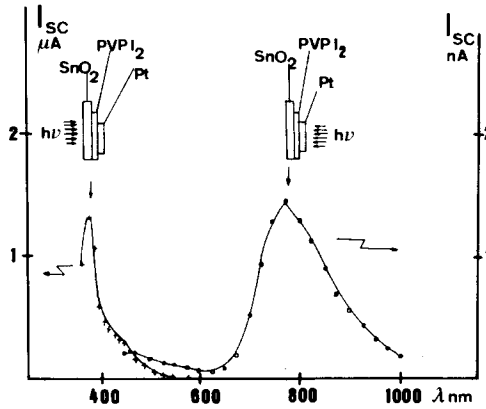


Fig. 6. Schematic representation of the cell.  $l$  = thickness of the polymer film;  $l_b$  = width of the contact barrier in the polymer.

sample thicknesses of 45  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively. An increase of photocurrent is also observed at shorter wavelengths. It thus appears that the region of the polymer which is essentially responsible of the photocurrent is in direct contact with the tin oxide layer. The small photocurrent observed at shorter wavelengths, when excitation is through the Pt gauze, confirms that an electrical barrier exists at the back contact. The sign of this latter photocurrent is the same as that for front face illumination and is thus consistent with the dark characteristic given in Figure 4. Incidentally, the sign of the photocurrent is independent of the irradiation side. This rules out the predominance of a Dember effect in these observations.

### DISCUSSION

The data obtained by back side irradiation can be treated in a similar way as that used previously by Ghosh et al. in his work on magnesium phthalocyanine.<sup>11</sup> Let us consider a model such that only the SnO<sub>2</sub>—polymer contact barrier is taken into account (Fig. 7). It can be shown<sup>10</sup> that the short circuit current is given by

$$I_{sc} = \phi I_{hv} \left\{ \frac{\alpha}{\alpha - \beta} \left[ \exp[-\beta(l - l_b)] - \exp[-\alpha(l - l_b)] \right] + \left[ \exp(-\alpha[l]) \left[ \exp(\alpha l_b) - 1 \right] \right] \right\} \quad (3)$$

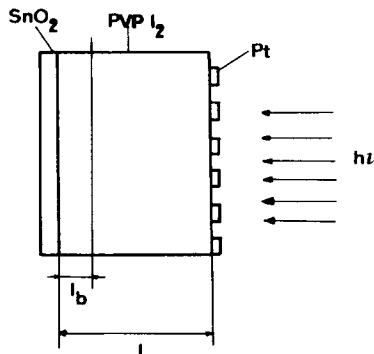


Fig. 7. Short-circuit photocurrent: irradiation through front contact (+—+—+); irradiation through back contact (⊖—⊖—⊖).

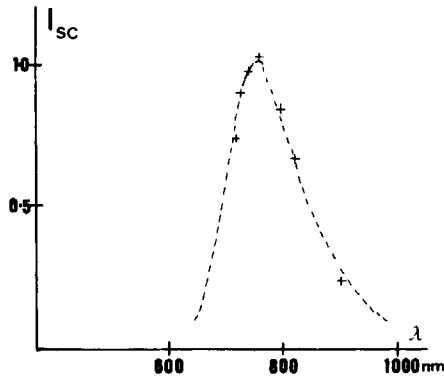


Fig. 8. Comparison between calculated (+) and measured  $I_{sc}$  values.

where  $\beta^{-1} = L$ , the diffusion length of the carriers,  $\alpha(\text{cm}^{-1})$  is the absorption coefficient,  $\phi$  is the quantum yield of carrier formation (considered here as wavelength independent), and  $I_{hv}$  is the light intensity ( $\text{cm}^{-2}$ ).

As discussed at the beginning of this paper,  $\alpha$  values could be measured accurately to the longest wavelengths; the analysis according to eq. (3) is thus limited to  $\lambda > 700$  nm. A comparison between calculated and measured  $I_{sc}$  values is given in Figure 8. The following set of parameters were used:  $l = 14.5 \times 10^{-4}$  cm;  $L = 7 \times 10^{-4}$  cm;  $l_b = 10^{-5}$  cm. The computed curve is very sensitive to the sample thickness  $l$ , but any value of  $l_b$  such that

$$l_b < 10^{-5} \text{ cm}$$

can be used without changing the fitting.

From the electrical characteristics recorded in the dark and under irradiation, a qualitative dependence of the electrical potential along the cell can be inferred (Fig. 9). It is remarkable that the photopotential decreases when the  $I_2$  content increases (Table I). Presumably, the increase of  $I_2$  (acceptor) lowers the Fermi level of the polymer and thus decreases the amount of charge transfer from PVP— $I_2$  to the  $\text{SnO}_2$  layer. On the other hand, under the same conditions, the photocurrent is increased, as can be expected if the light is absorbed in the vicinity of the  $\text{SnO}_2$  contact, e.g., in the space charge region.

As indicated above, X-ray diffraction reveals the amorphous character of the PVP— $I_2$  samples. The electrical properties are consistent with this observation. The optical gap ( $E_{op}$ ) measured by absorption spectroscopy or from the onset of the photoconductivity is 1.2 eV. The activation energy to electrical conduction ( $E_a$ ) around room temperature has been estimated previously<sup>12</sup>:

$$0.45 < E_a \text{ (eV)} < 0.57$$

With an average value of 0.51 eV it appears that

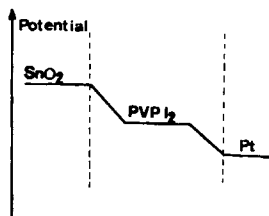


Fig. 9. Qualitative variation of the electrical potential along the cell.



$$E_a \cong E_{op}/2$$

as can be expected with an amorphous semiconductor in the high temperature range.<sup>13</sup> From capacitance-voltage measurements it appears that the width of the space-charge region is smaller than 50 Å. This is also consistent with the amorphous character of the polymer and with the results of application of eq. (3).

The transformation yield of "white light" ( $2 \times 10^{-3}$  W·cm<sup>-2</sup>) into electricity is 0.05%. This can be compared with the performance of other organic cells using magnesium phthalocyanine ( $\eta = 10^{-3}\%$ <sup>11</sup>), chlorophyll ( $\eta = 10^{-2}\%$ <sup>14</sup>), hydroxysquarylium ( $\eta = 10^{-1}\%$ <sup>15</sup>), and merocyanine dyes ( $\eta = 7 \times 10^{-1}\%$ <sup>16</sup>). Nevertheless, one should avoid drawing any quantitative conclusions from these data since the transformation yields may have been estimated at different light powers. Usually  $\eta$  decreases when the light intensity increases. What is perhaps most noticeable here is that a rather good transformation yield is obtained by combining a low  $V_{oc}$  value with a high  $I_{sc}$ ; the opposite situation usually prevails with high resistance organic materials.

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