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SEMICONDUCTING PHOTOCONDUCTORS FROM AMORPHOUS FILMS OF DYE-SENSITIZED POLYPHENYLACETYLENE

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Trans-polyphenylacetylene (PPA), in the form of amorphous films that are several μm thick, is a semiconducting photoconductor, both, undoped and doped with certain electron-accepting compounds. This report describes the photoconductivity in PPA sensitized with the dyes pyronin Y and methylene blue, which sensitize the photoresponse in the region of the dyes' absorption bands and desensitize it elsewhere. The major photoconductivity mechanism is concluded to be the injection of electrons that are photogenerated in the dye into the conducting states of the polymer, followed by transport through the polymer by a trap-modulated bandlike mechanism.

INTRODUCTION

Polyphenylacetylene (PPA), in the form of films which are 2 - 8 μm thick, is photoconductive, both, undoped and when doped with certain inorganic and organic electron-accepting compounds.[1,2] Trans-PPA is more photoconductive than the cis-isomer, and uniformly-doped, crack-free films are more readily prepared. The photoconductivity action spectra indicate a modest photoresponse in the region of the polymer's π-π^* transition (short wavelength photoconductivity) and better photosensitivity in the red and near-infrared beyond the π-π^* absorption edge of about 525 nm (long wavelength photoconductivity). Doping enhances the photosensitivity in both regions. These two regions are separated by a minimum located near the absorption edge. The long wavelength photoconductivity is attributable to photodetrapping from shallow traps in the undoped polymer;[1-3] in PPA doped with iodine or 2,3-dichloro-5,6-dicyano-pbenzoquinone (DDQ), the long wavelength photosensitivity sets in roughly where the charge transfer absorption begins to exceed that of the pure polymer.[1,2] The charge transfer bands are broad and extend into the near infrared.[4,5] The polymer-acceptor interaction which gives rise to these spectra depends on the polymer's isomeric structure, involves complexes of different stoichiometry and has so far only been analyzed in part.[2,3] Whatever the exact nature of the charge transfer complexes, they introduce intergap states which become the source, as well as sink of photocarriers[1,2] and probably of dark charge carriers as well.[6]

The short wavelength photoconductivity has not yet been studied in detail. Its enhancement in the doped polymer, outside of the charge transfer band, may be attributable to the interaction of charge carriers, or excitons, created in the short wavelength region with trapped charge originating from the charge transfer interaction.

At fields greater than about 10^4 V/cm, the dark current due to electrons begins to exceed the hole current, and undoped PPA behaves as an n-type semiconductor. The presence of strongly unipolar, trap-controlled, non-ohmic electron currents in undoped trans-PPA,[1] together with a study of photoconductivity parameters in undoped and acceptor-doped PPA, indicate that interactions of mobile electrons with shallow traps, as well as with recombination centers, play a key role in phototransport.[1,2] A description of phototransport must therefore distinguish between mobile and trapped carriers and the mechanism can be referred to as "trap-modulated bandlike transport." It is associated with short carrier lifetimes--microseconds in doped PPA and less in the undoped polymer[2]--compared to those characteristic of polyvinylcarbazole,[7] which is a photoconductive insulator.

The generation of mobile carriers in undoped PPA was concluded to occur by injection of charge carriers from high work function metal electrodes, such as Cr, Pd or Cu, into defect states in the bandgap of the polymer, from which electrons are promoted into the conducting states across a band or mobility edge, with holes strongly trapped; in acceptor-doped PPA, positive and negative carriers are created in approximately equal numbers by injection into conducting states from charge transfer states which act also as traps or recombination centers. Although the source of carriers lies outside the polymer in the first case and within it in the second, the physical models proposed for either case[2] involve an equilibrium between mobile states and traps (shallow and deep). The photocarrier generation and recombination kinetics can then be considered within the general framework of the band models proposed by Rose.[8] As shown by Rose, the exponent a relating the photocurrent density, J_{ph}, and the intensity of the absorbed light, I, in the expression J_{ph} = const I^a equals 0.5 for some common shallow trap distributions located above the Fermi level and in equilibrium with the conduction band. The data on the light intensity-dependence of J_{ph} in undoped and acceptor-doped PPA are generally consistent with that picture. In addition, the superlinear field dependence of J_{ph} suggests a high ratio of trapped to mobile charge,[1,2] as required by this type of model.

This paper deals with photoconductivity in dye-sensitized trans-PPA, whose photoresponse differs in significant respects from that described. Although this calls for some changes in the details of the physical model, the data appear to give further support to the concept that extended states play a significant role in the photoconductivity of this semiconducting conjugated polymer.

EXPERIMENTAL SECTION

The trans-PPA sample used in this study had been prepared with $W(CO)_6$ catalyst in CCl_4 solution under irradiation by a high pressure mercury lamp and obtained through the courtesy of Professor Higashimura, Kyoto University.[9] The polymer sample is room temperature-soluble and has an average molecular weight of 80,000, as measured by osmometry.[9] The dye samples, pyronin Y (PY) and methylene blue (MB) were obtained from Aldrich Chemical Company.

Dye sensitized polymer films were prepared by mixing dilute solutions of PPA and pigment, both in chloroform, followed by casting the mixture over NESA (SnO_2) glass slides. The thickness of the film was determined by weighing. Films of 3 - 6 μm were used in this study. The composition of the film could be calculated from the initial composition of the two component solutions and is represented as weight percent dye (Y). Due to their limited solubility in chloroform as well as their limited structural compatibility with the polymer, only about 2 weight percent of the dyes can be incorporated into the polymer without severe crack development or visible grain formation in the film. A thin Al layer of defined area (0.04 - 2 cm^2) was then vacuum deposited on top of the polymer film. In this manner, the film samples were in a diodelike or sandwich configuration of type $Al/PPA\text{-}dye/SnO_2$.

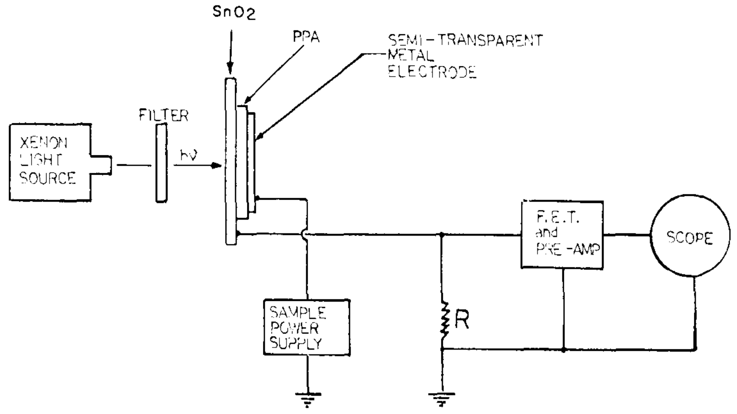


FIGURE 1 Experimental Arrangement

The experimental arrangement is shown in Figure 1. The continuous light source was a Schoeffel 150 W Xenon arc gas discharge lamp (Model L-124) with a Schoeffel LPS 251 HR power supply. The spectral distribution of the source was calibrated against a standard test silicon solar cell (NASA standard) under AMI conditions. The spectral content of the light source was varied by using 10 nm wide band pass filters (Oriel Corp.) and various cut-off and neutral density filters (Ealing Optics), whose spectral characteristics and transmittance had been determined spectrophotometrically. The voltage source was a dc Hewlett-Packard Model 6216A power supply which could put a positive or negative bias on the top electrode. Currents were fed into a FET converter-amplifier circuit and displayed on a Tektronix Model 466 storage oscilloscope. The field-dependent quantum yield is defined as $Q = J_{ph}/\phi e(1-T)$ where J_{ph} is the photocurrent density, e is the electronic charge, T is the fractional transmittance of the sample and ϕ is the photon flux.

RESULTS

The dark current-voltage characteristics for unsensitized trans-PPA as well as for PPA sensitized with pyronin Y (PY) and methylene blue (MB) are shown in Figure 2. In undoped PPA,

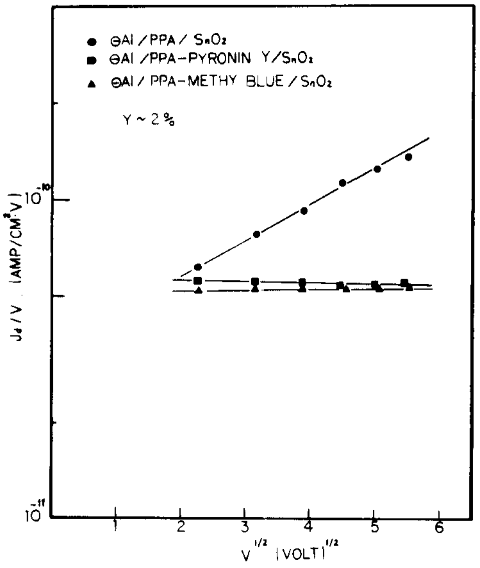
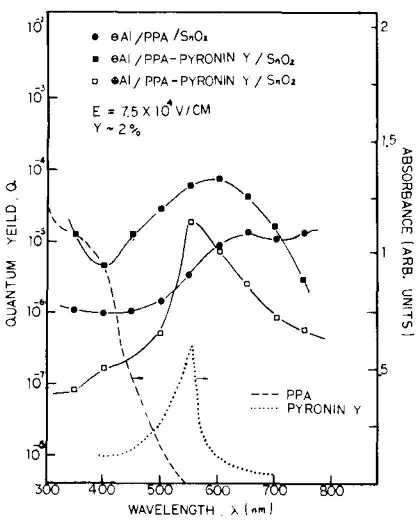


FIGURE 2 Dark Currents in Sensitized and in Unsensitized PPA

the dark currents (J_d) obey the Schottky-Richardson equation for diffusion-controlled, field-assisted thermionic emission ($J_d \alpha V^{3/2}$) when the metal electrode is negatively biased, whereas quasi-Ohmic dark currents are obtained with a positively biased metal electrode.[1] However, in dye sensitized PPA films, the negatively and positively biased dark currents are Ohmic and equal.

The photoconductivity action spectra and quantum yields for unsensitized trans-PPA, as well as for PPA-PY and PPA-MB are shown in Figures 3 and 4. The characteristics and interpretation of these spectra in the undoped polymer were outlined in the Introduction. Figures 3 and 4 show the enhancement of the photoconductivity in the dyes' adsorption bands under, both, positive and negative bias. In undoped PPA, virtually no photoconductivity is observed under positive bias and otherwise similar conditions.[1] In the PPA-PY complexes, a substantial enhancement of the photoconductivity



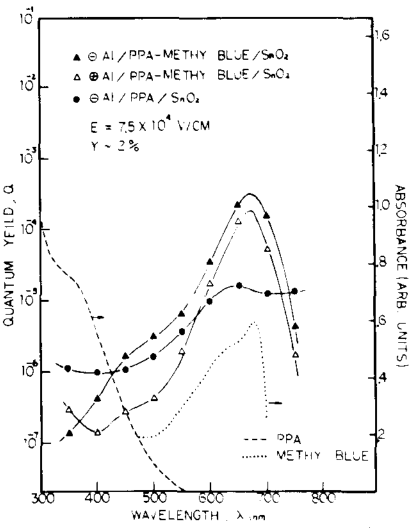


FIGURE 3 (left) Absorbance and Photoconductivity Action Spectra of PPA and PPA-PY

FIGURE 4 (right) Absorbance and Photoconductivity Action Spectra of PPA and PPA-MB

outside the region of maximum dye absorption was also observed when the metal electrode was under negative bias. However, the long wavelength photoconductivity characteristic of unsensitized PPA diminishes considerably upon incorporation of either dye. A comparison of the magnitude of photocurrents in the far visible and near-IR regions between pristine and dye-sensitized PPA is given in Figure 5.

Figures 6 and 7 illustrate, respectively, the intensity (I) dependence of the photocurrents in the region of dye absorption in PY and MB sensitized PPA films. The photocurrents in PPA-PY depend approximately linearly on light intensity when the metal electrode is under positive bias. However, upon reversing the bias, a significantly larger photocurrent which depends sublinearly on light intensity ($J_{ph} \alpha I^{0.7}$) is observed. In PPA-MB, the photocurrent vs. light intensity curve changes from approximately linear at low light intensities to a slightly sublinear form at high intensities, regardless of the bias on the metal electrode. In unsensitized PPA, the intensity exponent is always ≤ 0.5.[1,2]

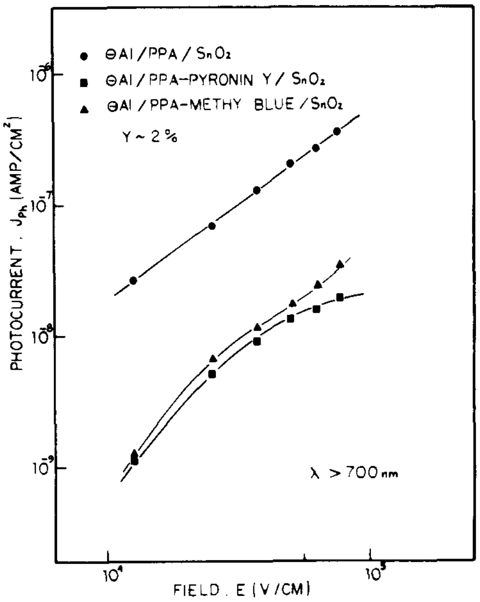


FIGURE 5 Field Dependence of Photocurrent in Sensitized and Unsensitized PPA

The field (E)-dependence of J_{ph} for PY-sensitized PPA obtained with both positive and negative bias on the top metal electrode is shown in Figure 8. The current under positive bias is slightly superlinear, indicating the presence of space charge perturbation. A stronger superlinear field dependence is observed when the metal electrode is under negative bias. The presence of a stronger space-charge-perturbed photocurrent in PPA-PY with the metal electrode under negative bias and the sublinear intensity dependence may be associated with some injection of electrons by the electrodes into shallow traps in the polymer (see Discussion).

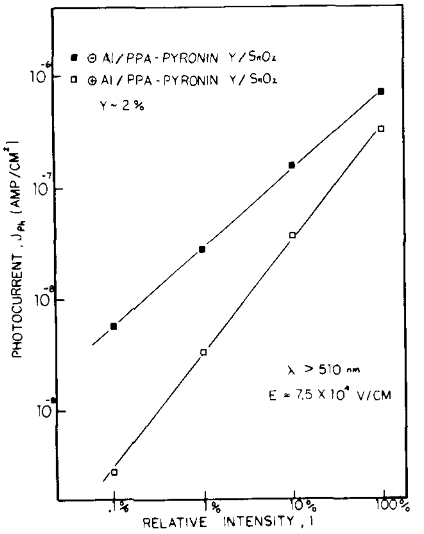
Table I summarizes the photoconductive properties, in terms of the photocurrent to dark current ratio, of dye-sensitized PPA in films that are approximately 3 μm thick. Both PPA-MB and PPA-PY are stable at the stated field and light intensity. The photoconductive gain can be increased considerably at a higher field and light intensity.

TABLE I (E = 7.5 x 10^4 V/cm; I $\sim$ 4 x 10^{16} photons/cm^2•sec

Sample	Wt.% Dye	Dark Current, J_d (Amp/cm^2)	Photocurrent, J_{ph} (Amp/cm^2, 510<λ<700 nm)	$\frac{J_{ph}}{J_d}$
PPA-PY	2%	1.7 x 10^{-9}	7.22 x 10^{-7}	425
PPA-MB	2%	1.7 x 10^{-9}	6.94 x 10^{-7}	408

DISCUSSION

Possible mechanisms for photocarrier generation in dye-sensitized organic and polymeric photoconductors have been discussed in the literature.[10-12] A distinction must be made between carrier generation in the polymer promoted by the transfer of excitation energy from the photoexcited dye (radiation and Förster energy transfer[13]) and injection of charge carriers created in the dye by light. The first of these mechanisms is unlikely to make the major contribution to carrier generation in the dye-sensitized PPA because of the weak overlap between the polymer and dye absorption bands whose maxima lie at 550 nm (PY) and 667 nm (MB), respectively. The additional possibility of energy transfer from the dye to



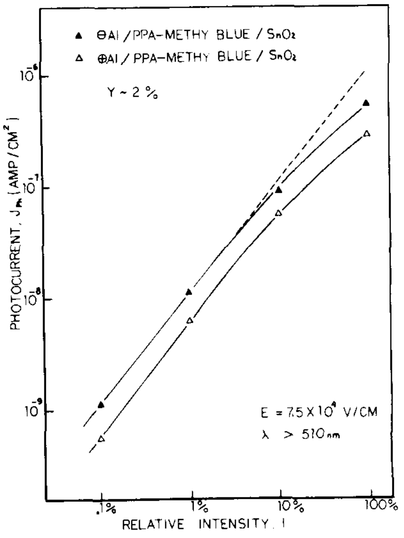


FIGURE 6 Light Intensity Dependence of Photocurrent in PPA-PY

FIGURE 7 Light Intensity Dependence of Photocurrent in PPA-MB

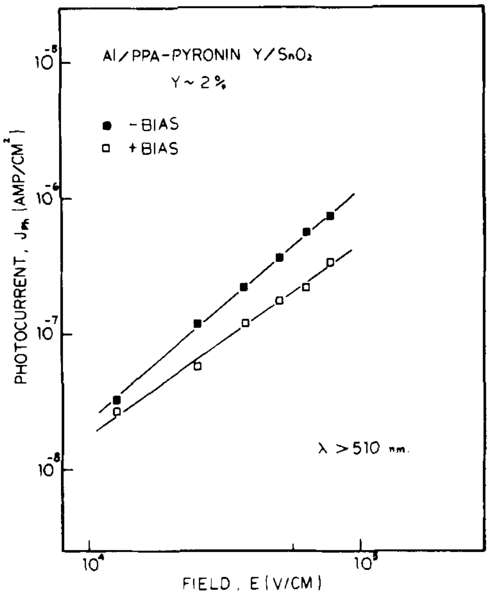


FIGURE 8 Field Dependence of Photocurrent in PPA-PY

trapped carriers must not be excluded. If, on the other hand, the charge injection mechanism is operative, both the sensitization efficiency and the spectral response must be characteristic of the sensitizer alone and not of the photoconductor, with the latter serving only as a transport medium. Figures 3 and 4 clearly indicate that the spectral response in PY- and MB-sensitized PPA is, in fact, characteristic of the sensitizers and not of the photoconductive transport medium. The appearance of positively biased photocurrents in PPA-PY and PPA-MB systems and their exact correspondence with the absorption spectra of the dyes, the disappearance of the near-IR photoconductivity upon dye sensitization, and the increase in the intensity exponent from ≤ 0.5 in pristine PPA[1,2] toward about 1 in PPA-PY and PPA-MB are all different from the inherent photoconductive response of the polymer. Thus, the present experimental observations generally support the view that dye sensitization in PPA involves the initial creation of excited carriers (electrons) in the pigment, followed by their injection into the conduction states of the polymer.

An approximately first-power dependence of J_{ph} on the light intensity, I, is consistent with carrier injection from the excited dye into the conduction states of the polymer, followed by carrier drift to the opposite electrode in the presence of permanent traps, but in the absence of shallow traps, such that space charge free (SCF) conditions are maintained. These conditions appear to be approached in PPA-MB, except at high light intensity under either bias (Fig. 7), and in PPA-PY, under positive bias only (Fig. 6). SCF conditions are, however, not likely to be maintained, if electrons are also injected from the electrode into trapping states lying in the bandgap of the polymer, a mechanism that accounts for the photoconductivity in undoped PPA.[1,2] In the presence of electron exchange between shallow traps and conduction states, the light intensity exponent of J_{ph} lies in the range of 0.5 to 1.0.[8] The data on the I-dependence of J_{ph} in negatively-biased PPA-PY, together with the greater magnitude of the negatively-biased photocurrent, therefore support the view that, in this case, electron injection from the electrode into defect states in the polymer's bandgap contributes to the photocurrent, as does, conceivably, energy transfer to the trapped electrons. The more strongly superlinear field-dependence of J_{ph} in negatively-biased PPA-PY (Fig. 8) may also be cited in support of electron injection into defect states.

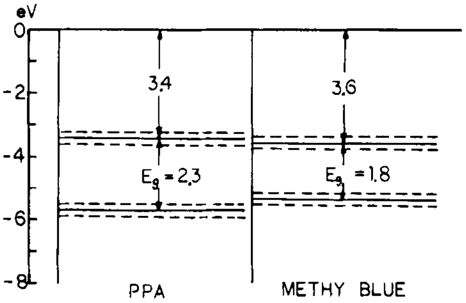


FIGURE 9 Energy Levels in PPA-MB

The proposed mechanism of electron injection from the dye into the polymer requires that the excited state of the dye lie above the polymer's conduction states. Figure 9 is the proposed energy diagram of the PPA-MB interface based on the best currently available ionization potentials of PPA[3] and the dye.[14] Although the dye's conduction band edge appears at 0.2 eV below that of the dye, some uncertainty in the parameters chosen and the probable diffuseness of the bandedges[15] allow us to offer the energy diagram of Figure 9 in support of the proposed injection mechanism. The marginal energy content for injection into PPA of the dye's excited state might, in fact, be offered in support of the further observation of an apparent incipient saturation phenomenon in PPA-MB, where J_{ph} becomes sublinear in I at high I (Figure 7). This phenomenon is absent with PY, a more p-type dye,[14] again in support of the mechanisms proposed.

CONCLUSION

The spectral response of polyphenylacetylene can be controllably modified and significantly enhanced by sensitization with organic dyes. In the region of dye absorption, the photoconductive response of PPA can be increased by at least one order of magnitude, at least for the two types of dye studied. The mechanism of spectral sensitization is consistent with charge (electron) transfer from excited dye molecules to the conduction states of the polymer and/or the transfer of excitation energy from the dye molecules to trapped carriers in trapping states. The latter is probably operative only in the presence of electron injection from the electrode into the trapping states of the polymer. Distinction between these two mechanisms requires a careful study of the temperature dependence of the photocurrent. In case of direct charge transfer, the photocurrent should be nearly independent of temperature,[16] and in case of excitation energy transfer to trapped carriers, a strong temperature dependence should be observed.[8]

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