

# Electrophotographic photoreceptor devices incorporating polyphenylacetylene sensitized by crystal violet

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## Abstract

The photosensitivity of electrophotographic photoreceptor (PR) devices incorporating polyphenylacetylene can be more greatly enhanced by sensitizing with crystal violet (CV) and employing complex transfer layer consisting of polyvinyl carbazole (PVK), triphenylamine (TPA) and polycarbonate (PC). The PR device with Al/ct-*cis*-transoidal polyphenylacetylene (PPA): CV: poly(methyl methacrylate) (100:5:10)/PVK:TPA:PC (10:10:1) appeared preferable in photosensitivity enhancement and showed good photosensitivity: initial surface potential,  $V_{\max} > 800$  V; residual surface potential  $V_{\min} < 20$  V; dark decay,  $RD < 10$  V s<sup>-1</sup>; photodischarge,  $\Delta V_{t=0.5s} = 85\%$  and  $\Delta V_{t=0.1s} = 90\%$ ; half-decay time  $T_{1/2} = 0.23$  s; photosensitivity  $S \approx 4.35$  s<sup>-1</sup>. A mechanism of high photosensitivity in CV-sensitized PPA is proposed.

**Keywords:** Electrophotographic photoreceptor; Polyphenylacetylene; Crystal violet

## 1. Introduction

Polyphenylacetylene (PPA) is a conjugated polymer with *cis*- and *trans*-configuration double bonds. Kang and coworkers [1–3] reported that *trans*-PPA is a semi-conducting photoconductor when it is either doped with iodine (I<sub>2</sub>) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and sensitized with the dyes pyronin or methylene blue. Recently, we reported that irradiating with <sup>60</sup>Co-ray and electron beam, doping with I<sub>2</sub> and FeCl<sub>3</sub>, and sensitizing with 4-isothiocyanatofluorescein (F-II) or 2,4,7-trinitro-9-fluorenone (TNF) can convert *cis*-PPA to highly photosensitive materials [4–6]. This paper describes the photosensitivity of an electrophotographic photoreceptor (PR) device incorporating *cis*-PPA sensitized with crystal violet (CV) (a kind of dye) for the first time. The effects of different constitutions, compositions and thicknesses of the PR device on the photosensitivity have been investigated by means of potential discharge techniques. At the same time, a mechanism of high photosensitivity in PPA sensitized with CV is proposed.

## 2. Experimental details

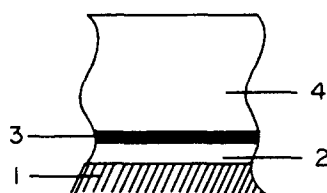
### 2.1. Preparation of polyphenylacetylene

PPA was prepared according to the method described previously [4]. The number-average molecular weight is about 10<sup>5</sup> as measured by gel permeation chromatography. The *cis* content of the PPA is more than 90%. *cis*-PPA has two isomers: *cis*-*cis*oidal and *cis*-*trans*oidal, which were separated by dissolving in tetrahydrofuran (THF) then filtering. The *cis*-*trans*oidal PPA (ct-PPA) was obtained by precipitation from THF solution into methanol, which was used in this study and given as PPA below.

### 2.2. Electrophotographic photoreceptor device

The PR devices incorporating CV-sensitized PPA consisted of several layers: an aluminium substrate, a poly(methyl methacrylate) (PMMA) barrier layer (BL) or not, a PPA/CV/PMMA charge generation layer (CGL), and a polyvinylcarbazole (PVK) (triphenylamine) (TPA) polycarbonate (PC) charge transport layer (CTL). Each of the layers was solution coated and dried at 40 °C under vacuum before adding successive layers. A cross-sectional view of the PR device is shown

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1. Aluminium Substrate
2. Barrier Layer (BL)
3. Charge Generation Layer (CGL)
4. Charge Transport Layer (CTL)

Fig. 1. Cross-sectional view of PR device: 1, aluminium substrate; 2, BL; 3, CGL; 4, CTL.

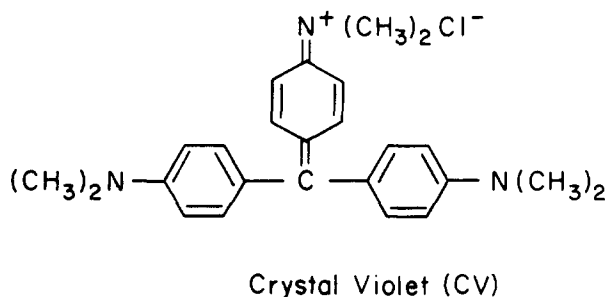


Fig. 2. Sensitizer used for the CGL.

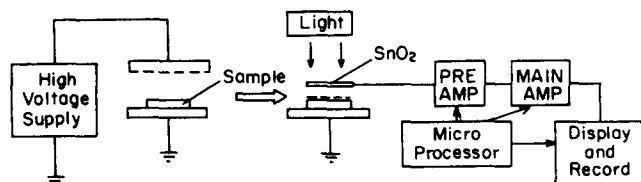


Fig. 3. Experimental arrangement for photosensitivity studies.

in Fig. 1. The sensitizer used for the CGL is illustrated in Fig. 2.

### 2.3. Measurement

The technique used in photosensitivity studies employs the photoinduced discharge of the corona-charged sample. A schematic diagram of the experimental arrangement is shown in Fig. 3. The sample was charged to a negative potential by the corona discharge and then exposed under a 5 W lamp (white light). The surface potential discharge curves were recorded with a Z-80 microprocessor system.

The *cis* content of PPA was determined according to [4] from IR spectra recorded on a Nicolet-5DX Fourier transform IR spectrophotometer. GPC measurements were performed at 30 °C on a Waters GPC model 208. The reference was polystyrene. The UV spectra were recorded on a Shimadzu UV-240 UV spectrophotometer. The thickness of PR devices were

determined by a Minitest 2000 thickness measurer (E.P.K.Co., Germany).

### 3. Results and discussion

In general, the high photosensitivity of a material is characterized by low dark decay, high discharge and low residual potential. The photosensitivity is always characterized by the reciprocal of the half-decay time. Fig. 4 shows typical photoinduced discharge curves (PIDCs) of negatively charged samples: a CV-sensitized PPA PR device in Fig. 4(a) and an unsensitized device in Fig. 4(b). It can be seen from Fig. 4 that the photosensitivity in the CV-sensitized PPA P/R device is much higher than that in the unsensitized device; it is well known that sensitizing enhances the photosensitivity of PPA.

It has been found that the CV content in PPA has an important influence on the photosensitivity of PR devices incorporating PPA as shown in Table 1. There is little photosensitivity in the PR device containing wholly PPA (i.e. 0% CV) or in a device containing 100% CV. The photosensitivity enhances rapidly with increasing CV content and reaches a plateau after wt.5% CV in PPA. The PR devices incorporating PPA sensitized with CV show a high initial surface potential, high photodecay and very good photosensitivity compared with the device sensitized with fluorescein-II and TNF [5].

Putting resin in a PR device can improve its coherent and mechanical properties. The effects of PMMA in the CGL and PC in the CTL on the photosensitivity of the PR device are shown in Fig. 5 and Fig. 6 respectively. It can be seen from Fig. 5 that with increasing PMMA content in the CGL the initial surface potential and residual surface potential are enhanced but the photosensitivity of the PR device decreases.

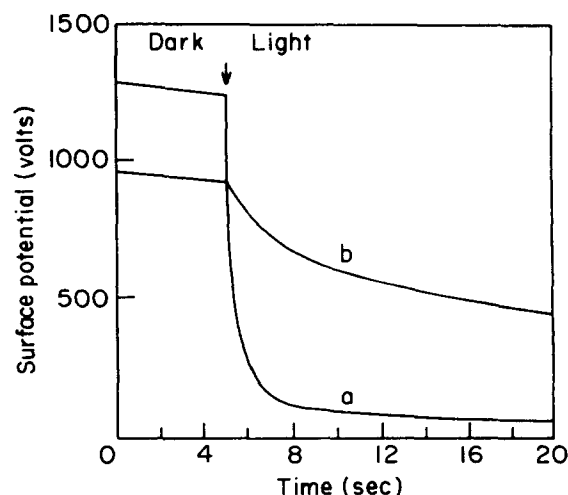


Fig. 4. Typical PIDCs for negatively charged PR devices: (a) Al/PPA:CV:PMMA/PVK:TPA:PC; (b) Al/PPA:PMMA/PVK:TPA:PC.

Table 1  
Photosensitivities of photoreceptor devices with various crystal violet content

CV <sup>a</sup> x (wt.%)	V <sub>max</sub> (V)	V <sub>min</sub> (V)	RD (V s <sup>-1</sup> )	ΔV <sub>t=0.5s</sub> (%)	ΔV <sub>t=1s</sub> (%)	T <sub>1/2</sub> (s)	S (s <sup>-1</sup> )
0	423	279	8.8	4.4	7.6		
0.5	670	42	2.5	55.8	71.2	0.46	2.17
1.0	780	58	6.0	62.4	75.9	0.38	2.63
2.0	862	38	6.0	68.5	80.4	0.30	3.33
5.0	890	14	7.0	84.2	91.4	0.23	4.35
10.0	1216	20	13.0	84.9	90.7	0.23	4.35
100.0 <sup>b</sup>	1372	420	13.0	7.3	14.0		

<sup>a</sup>PR device: AL/PPA:CV:PMMA(100:x:10)/PVK:TPA:PC(10:10:1).

<sup>b</sup>PR device:AL/PPA:CV:PMMA(5:100)/PVK:TPA:PC(10:10:1)

Note that samples are under a 5 W lamp exposure. / indicates a layer. CV: CV content in PPA; V<sub>max</sub>, initial surface potential; V<sub>min</sub>, residual surface potential; RD, dark decay; ΔV<sub>t=0.5s</sub>, discharge for 0.5 s; ΔV<sub>t=1s</sub>, discharge for 1 s; T<sub>1/2</sub>, half-decay time; S, material photosensitivity, reciprocal of the half-decay time.

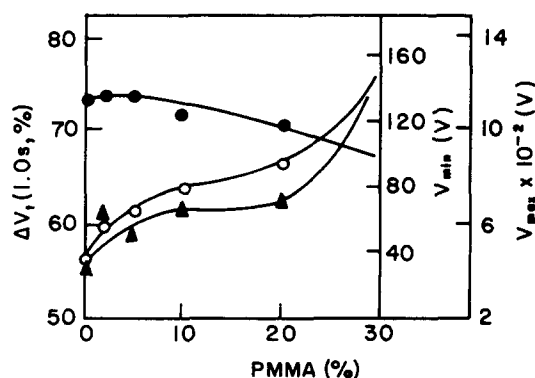


Fig. 5. Effect of PMMA content in the CGL on the photosensitivity (PR device: AL/PPA:CV:PMMA(100:1:x)/(PVK:TPA:PC(10:10:1)): ●, ΔV<sub>t</sub> vs. PMMA; ○, V<sub>max</sub> vs. PMMA; ▲, V<sub>min</sub> vs. PMMA.

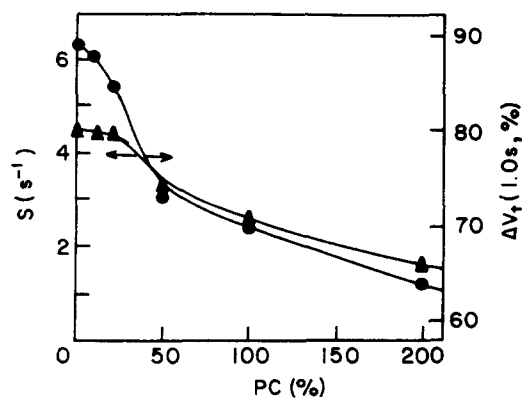


Fig. 6. Effect of PC content in the CTL on the photosensitivity (PR device: AL/PPA:CV:PMMA(100:2:5)/PVK:TPA:PC(100:100:x)): ●, ΔV<sub>t</sub> vs. PC; ▲, S vs. PC.

The optimum PMMA content was 10 wt.% in PPA. It is seen from Fig. 6 that the photosensitivity of the PR device decreases by increasing the PC content in the CTL. The optimum content was 10 wt.% in PVK.

When using PVK as the CTL material only, the V<sub>max</sub> of the PR device was very low because of the very thin CTL. When using TPA only, it may crystallize out and result in worse surface properties and sensitivity. When they are combined as the CTL, a PR device with high photosensitivity and better film-forming properties can be obtained. From Fig. 7, it is observed that the best TPA-to-PVK weight ratio is 1. When the weight PVK ratio is greater than 2, TPA begins to crystallize, and ΔV<sub>t</sub> and V<sub>max</sub> to decrease, i.e. the photosensitivity decreases.

It has been found that adding the sensitizer during the fabrication of a PR device incorporating PPA is a good way to induce PPA to show high photosensitivity. However, there is an important influence of the different constitutions of the PR device on the photosensitivity enhancement, as shown in Table 2. It can be seen that the fourth structure Al/PPA:CV:PMMA(100:5:10)/PVK:TPA:PC(10:10:1) showed the best photosensitivity enhancement, i.e. an initial surface potential V<sub>max</sub> of 890 V, a residual surface potential V<sub>min</sub> of 14 V, a dark decay (RD) of 7 V s<sup>-1</sup>, a discharge percent ΔV of 91.4% for 1 s, a half-decay time T<sub>1/2</sub> of 0.23 s, and a photosensitivity of 4.45 s<sup>-1</sup>. A characteristic of this PR device is that there is no barrier layer.

The photosensitivity of the PPA PR device is very dependent on the thickness of the various layers in the PR device. It is seen from Fig. 8 that the optimum thickness of the CGL is 1.3 μm (as seen in Fig. 8, curve 2) and that of the CTL ranges from 15 to 20 nm.

With different exposed light wavelengths, the photosensitivities of the device are different. Fig. 9 indicates that the photosensitivity of the PR device is highest at 580–600 nm, the maximum absorption region of CV.

Fig. 10 shows the UV spectra of PPA with different CV contents. It can be seen that, with increasing CV

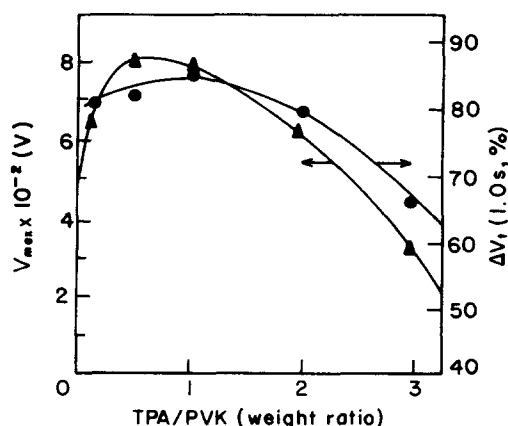


Fig. 7. Effect of the TPA-to-PVK ratio in CTL on the photosensitivity (PR device: AL/PPA:CV:PMMA(100:5:10)/PVK:TPA:PC(10:10:1)): ●, ΔV<sub>t</sub> vs. the TPA-to-PVK ratio; ▲, V<sub>max</sub> vs. the TPA-to-PVK ratio.

Table 2  
The photosensitivities for photoreceptor devices with different structures

Number	Structure of PR device <sup>a</sup>	$V_{\max}$ (V)	$V_{\min}$ (V)	RD ( $V s^{-1}$ )	$\Delta V_{t=0.5s}$ (%)	$\Delta V_{t=1s}$ (%)	$T_{1/2}$ (s)	$S$ ( $s^{-1}$ )
1	Al/CGL	62	31					
2	Al/CTL	562	374					
3	Al/BL/CGL	169	87					
4	Al/CGL/CTL	890	14	7.0	82.4	91.4	0.23	4.45
5	Al/BL/CGL/CTL	924	108	5.0	56.9	70.0	0.38	2.63
6	Al/CGL/CTL/BL	930	80	6.0	62.3	74.1	0.30	3.33
7	Al/CTL/CGL	726	222	15.0	19.8	30.3	3.38	0.30
8	Al/BL/CTL/CGL	816	272	6.0	17.3	28.0	3.30	0.30
9	Al/CTL/CGL/BL	866	194	14.0	29.0	41.6	1.61	0.62

<sup>a</sup>BL, PMMA; CGL, PPA:CV:PMMA (100:5:10); CTL, PVK:TPA:PC(10:10:1).

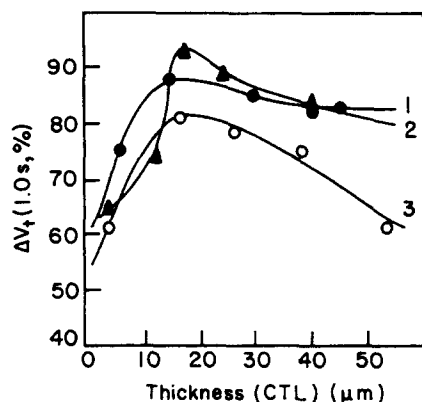


Fig. 8. Effect of thickness of the CTL on the photosensitivity at different CGL thicknesses: curve 1, ●, 0.6  $\mu\text{m}$ ; curve 2, ▲, 1.3  $\mu\text{m}$ ; curve 3, ○, 2.8. The PR device is the same as in Fig. 7.

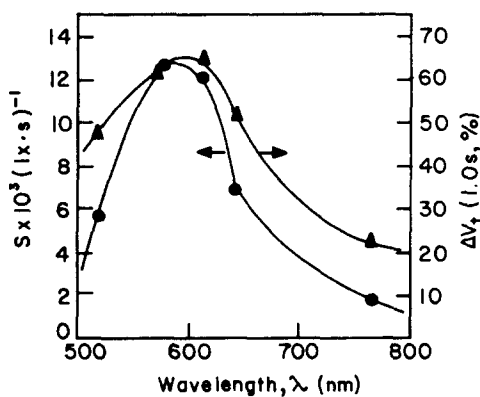


Fig. 9. Effect of the wavelength of exposed light on the photosensitivity: ●,  $S$  vs  $\lambda$ ; ▲,  $\Delta V_t$  vs.  $\lambda$ . The PR device is the same as in Fig. 7.

content in PPA, the absorption intensity at the maximum absorption of CV (585.5 nm) increases linearly (Fig. 11). No additional absorption peaks were observed. Thus the possible mechanism of high photosensitivity in CV-sensitized PPA may be spectral sensitization only.

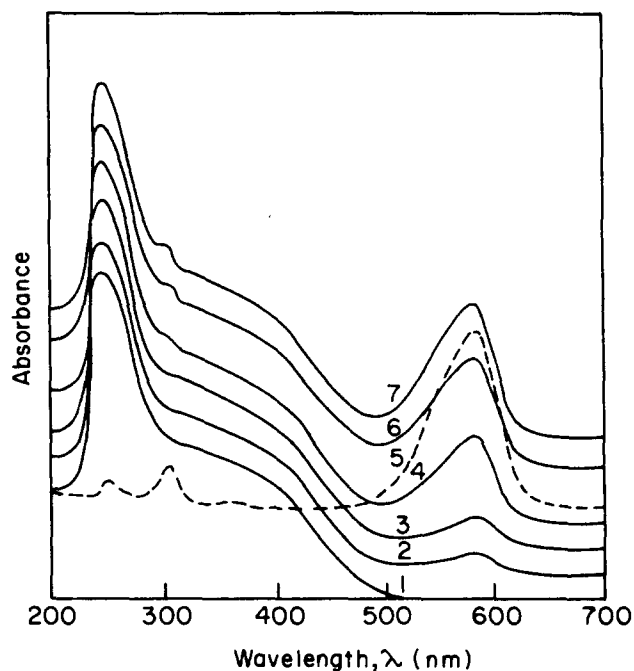


Fig. 10. UV spectra of PPA-CV solutions for the following CV contents in PPA: curve 1, PPA; curve 2, 1 wt.%; curve 3, 2 wt.%; curve 4, 5 wt.%; curve 5, CV; curve 6, 7 wt.%; curve 7, 10 wt.%.

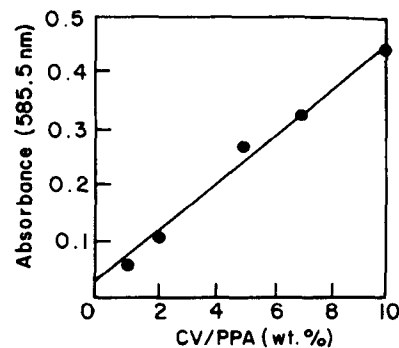


Fig. 11. Absorbance (585.5 nm) vs. CV content in PPA.

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