Synthesis and Photoconductivity Study of Phthalocyanine Polymers. III. PVK–CuPc(NO$_2$)$_2$

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SYNOPSIS

Cu–dinitro–diamine phthalocyanine was synthesized, the corresponding diazonium salt was reacted with vinylcarbazole (VK), and a novel polyvinylcarbazole (PVK)-bonded CuPc(NO$_2$)$_2$ (I) was synthesized. The chemical structure of polymer (I) is identified by elemental analysis and IR and UV/VIS spectroscopy. Polymer (I) contains about 21 mol % CuPc(NO$_2$)$_2$ rings that are covalently bonded to PVK. Polymer (I) shows good photoconductivity, which is much better than that of the corresponding phthalocyanine monomers. The influence of the interface layer and the charge-transportation material on the photoconductivity of polymer (I) is also discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Phthalocyanine compounds are typical organic photoconductive materials because of their broad infrared and visible region response. But their insolubility and difficulty in film-forming prevent further detailed study. Synthesis of phthalocyanine polymers is one way to improve solubility and film-forming. So far, several papers have reported the synthesis of phthalocyanine polymers[1] and studied their catalytic and electronic properties. However, there are few studies on their photoconductivity. Therefore, synthesis of phthalocyanine polymers and study of their photoconductivity bear great theoretical importance and applied value.

We have synthesized two novel phthalocyanine polymers and studied their photoconductivity.[2] The present paper describes the synthesis of a new polymer of polyvinylcarbazole (PVK)-bonded CuPc(NO$_2$)$_2$ [PVK–CuPc(NO$_2$)$_2$] (I) and a preliminary investigation of its photoconductive properties.

EXPERIMENTAL

1. Materials and Equipment

CuCl, urea, phthalic anhydride (PA), vinylcarbazole (VK), triphenylamine (TPA), and the other reagents were commercially available and of analytical grade. Polyvinylcarbazole (PVK) and N,N',N,N'-tetraphenylbensidine (TPD) were synthesized in our laboratory according to published procedures.[3,4]

IR spectra were recorded on an NIC-5DX Fourier transform infrared spectrometer. UV/VIS spectra were taken on a DU-50 spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240C elemental analyzer (see Table I). Photoconductive properties were performed on a GDT-I model photoconductivity measuring device.

2. Synthesis of 3-Nitrophthalic Acid

The synthesis is described in Ref. 5.

3. Synthesis and Reduction of Tetranitro Copper Phthalocyanine

The synthesis and reduction are described in Refs. 2a and 6.

Table I Elemental Analytical Data of CuPc Content in Polymer (I)

	Analysis	CuPc Contents (mol %)
C%	74.81	21.01
N%	12.95	20.32

4. Synthesis of PVK-bonded CuPc(NO₂)₂[1-2]

Ten grams of VK, the diazonium salt of 6.4 g dinitro-diamine CuPc, and 0.2 g of dodecyl sodium sulfate were mixed in a 250 mL round-bottomed flask and allowed to stand for 0.5 h at 0–5°C. Then, 0.1 g of 2,2'-azobisisobutyronitrile (AIBN) was added, and the reaction mixture was heated to 60°C for 5 h. The product was centrifuged in 200 mL of water, the supernatant liquid decanted, and the precipitate collected, washed with water, and then extracted in benzene for 48 h and dried at room temperature in vacuum. The PVK-bonded CuPc(NO₂)₂ (I) was obtained in 38% yield.

The infrared spectrum (KBr) of polymer (I) shows the typical absorption bands of phthalocyanine polymer at 1335, 1170, 1120, 1095, 905, 805, and 740 cm⁻¹. The UV/VIS spectrum (THF) is as follows:

672.0 nm (Abs. 1.576)
341.0 nm (Abs. 0.897)
250.0 nm (Abs. 0.801)
244.0 nm (Abs. 0.807).

5. Preparation of a Double-layered Photoreceptor Device and Photoconductivity Measurement[2,7]

The double-layered photoreceptor device (P/R) was made by coating an interface layer (IFL) of poly(methyl methacrylate) (PMMA), a charge-generation layer (CGL) of PVK-bonded CuPc-(NO₂)₂ (I), and a charge transportation layer (CTL) of TPD–PVK, TPA–PVK, or TPD–TPA–PVK on an aluminum plate, in that order.

A GDT-I model photoconductivity measuring device was used with a 5 W, 24 V visible lamp as a light source to plot the photoinduced discharge curve (PIDC) of the P/R. In this measurement, the surface of the P/R was negatively charged, and charge carriers were generated in CGL and injected into CTL under exposure. From PIDC, we obtained $\Delta V_1\%$, which is the percentage of potential discharge after 1 s of exposure, and $t_{1/2}$, which is the time from the original potential to half under exposure. The $t_{1/2}^{-1}$ can indicate photosensitivity. The bigger the $t_{1/2}^{-1}$, the higher the photosensitivity.

RESULTS AND DISCUSSION

1. Synthesis of PVK-bonded CuPc(NO₂)₂

PVK-bonded CuPc(NO₂)₂ was synthesized in the following way:

$$CuPc(NO_2)_2(NH_2)_2 \xrightarrow[\text{0-5°C}]{\text{HNO}_2/\text{HCl}} CuPc(NO_2)_2(N_2Cl)_2$$

$n/(n + m) = 0.21$

(I)
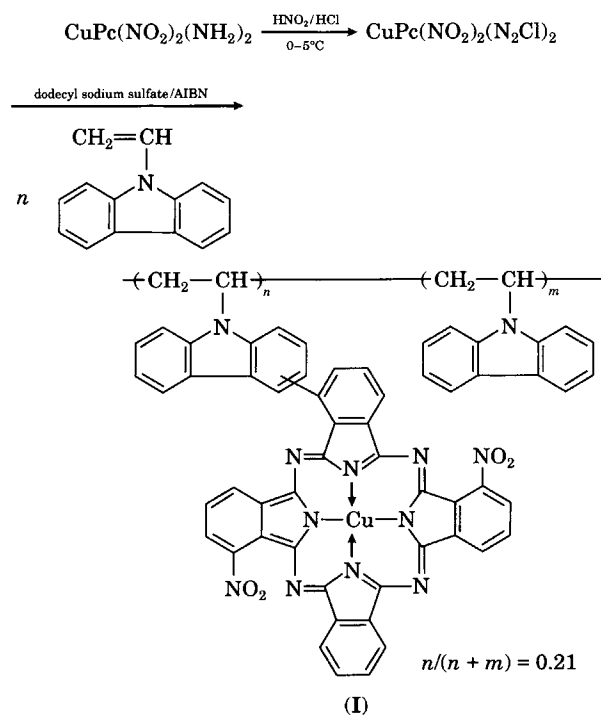
Table II Photoconductivity of Polymer (I), CuPc (NO₂)₄, and CuPc

CGM	V_0 (V)	V_R (V)	R_d (V/s)	R_p (V/s)	$\Delta V_1\%$	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (1/s)
Polymer (I)	714	38	22	420	60.6	0.76	1.32
CuPc (NO₂)₄	463	102	14	108	24.2	4.25	0.24
CuPc	598	200	18	142	26.4	4.84	0.21
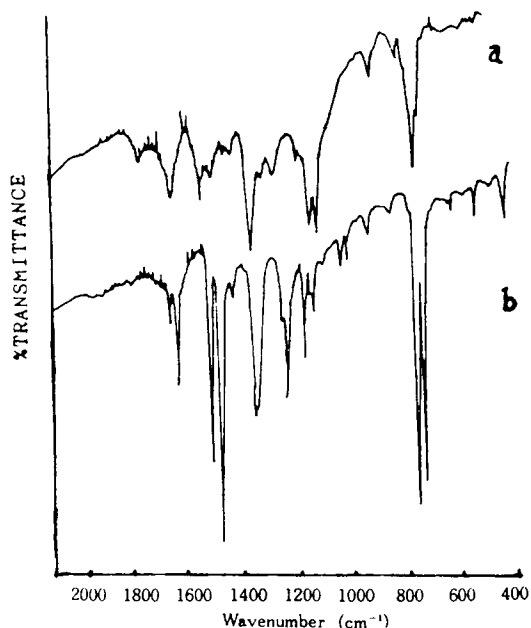
Figure 1   IR spectra of polymer (I) and PVK: (a) polymer (I); (b) PVK.

Figure 2   UV/VIS spectra of (------) polymer (I), (- · - ·) PVK, and (———) CuPc(NO$_2$)$_4$. Solvent: THF.

Figure 1 is the IR spectra of PVK and polymer (I). We find that polymer (I) shows absorption bands at 1335, 1170, 1120, 1095, 905, 805, and 740 wavenumbers, which are the typical absorptions of phthalocyanine. From the UV/VIS spectra of polymer (I), PVK and CuPc(NO$_2$)$_2$ (Fig. 2), we also find that pure PVK absorbs only in the violet region (200–400 nm), whereas the absorbances of polymer (I) expands to the visible region. It has a maximum peak at 672 nm, which is due to the existence of phthalocyanine. These indicate that CuPc(NO$_2$)$_2$ is, indeed, covalently bonded to PVK. Table II shows the CuPc content in polymer (I). We can see that the content of CuPc determined from the analytical data of carbon (21.0%) agrees with that from the analytical data of nitrogen (20.3%). Therefore, we may say that we obtain a novel PVK bonding at about 21 mol % CuPc(NO$_2$)$_2$ rings.

2. Photoconductivity of Polymer (I) [PVK-CuPc(NO$_2$)$_2$]

Figure 3 is the photoinduced discharge curve (PIDC) of P/R from polymer (I), CuPc(NO$_2$)$_4$, and CuPc. We find that polymer (I) has a high charge acceptance (V_0 = 714 V), a small rate of dark discharge (R_d = 22 V/s), a fast rate of photodischarge (R_p = 420 V/s), and a short time of half-discharge ($t_{1/2}$ = 0.76 s). These indicate that polymer (I) exhibits good photoconductivity. Compared with that
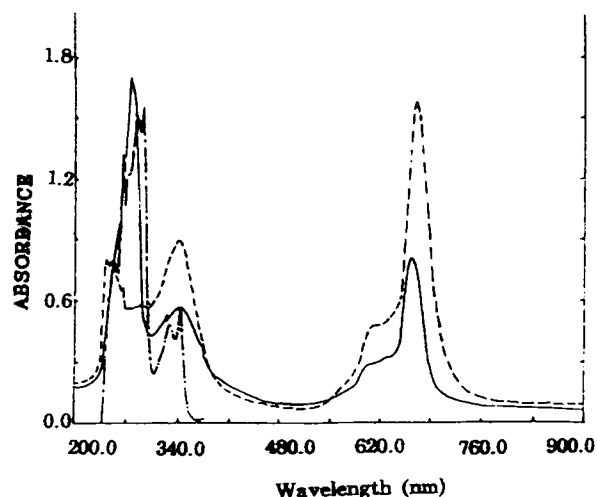
of CuPc and CuPc(NO$_2$)$_4$ monomers, we can see that polymer (I) has the advantages of larger values of R_p, $\Delta Vi\%$ (60.6%), and $t_{1/2}^{-1}$ (1.32 1/s) and a much lower value of V_R (38 V), showing much better photoconductivity than that of CuPc and CuPc(NO$_2$)$_4$ monomers.

From the structure of polymer (I), we can see that a huge π conjugated system is formed between CuPc(NO$_2$)$_2$ and the PVK main chain, which could
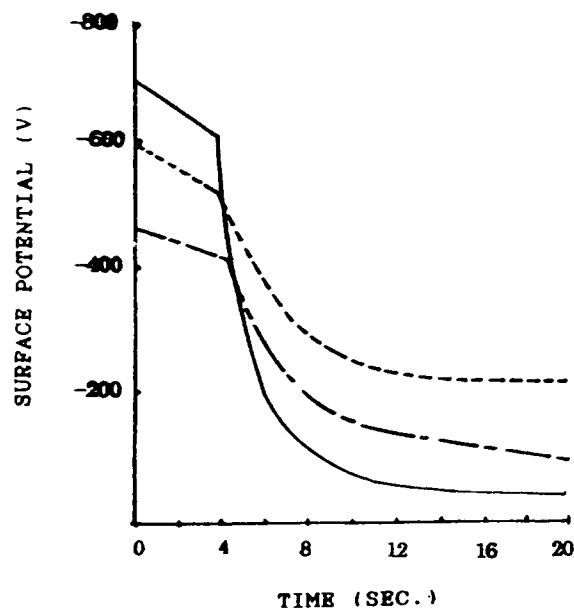

**Figure 3**   Photoinduced discharge curve of P/R from (———) polymer (I), (— — — —) CuPc(NO$_2$)$_4$, and (------) CuPc. CTM is TPD : PVK : PMMA = 5 : 2.5 : 1.

Table III Influence of IFL on the Photoconductivity of Polymer (I)

| IFL	V_0 (V)	V_R (V)	R_d (V/s)	R_p (V/s)	$\Delta V_1\%$	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (1/s)
None	460	35	23	178	47.2	1.07	0.93
1.2 μm	714	38	22	420	60.6	0.76	1.32
3.0 μm	1232	28	39	757	65.4	0.69	1.45
4.3 μm	1248	20	49	765	63.9	0.69	1.45

CTM is TPD : PVK : PMMA = 5 : 2 : 5 : 1.

enhance the charge carriers in the polymer chain through the carbazole groups and increase its photoconductivity. The other explanation for increasing photoconductivity is that the charge-transfer complex (CTC) may be formed between donor

$$\text{(amine group :N---)}$$
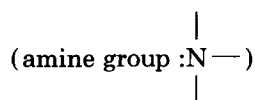
and acceptor (nitro group). We know that high photosensitivity is based on strong molecular interactions. Therefore, the formation of CTC can change the molecular interaction in polymer (I) and results in increasing the photoconductivity of this polymer.

From the above analyses, there are three characteristics in polymer (I): (a) A huge π conjugated system is formed between CuPc(NO$_2$)$_2$ and the PVK main chain, which may help electrons move more easily; (b) CTC may be formed between electron donor

$$\text{(amine group :N--- on the PVK main chain)}$$
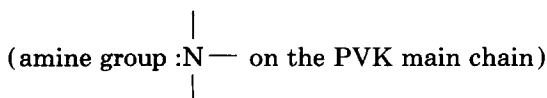
and electron acceptor (nitro group —NO$_2$ on the CuPc ring); and (c) charge generation material (phthalocyanine) and charge transportation mate-

rial (PVK) exist in the same polymer, which may decrease the surface energy potential between CGL and CTL and increase the injection efficiency of charge carriers. These three points may be used to explain the excellent photoconductivity of polymer (I).

3. Influence of Interface Layer on the Photoconductivity of the Polymer (I)

Table III reveals the influence of the interface layer (IFL) on the photoconductivity of polymer (I). We find that, under the same experimental conditions, with increase of the thickness of IFL, there is a steady rise in the surface potential acceptance (V_0), the rates of dark and photodischarge (R_d and R_p), but that $\Delta V_1\%$ and $t_{1/2}^{-1}$ increase rapidly at first, then remain almost unchanged. Therefore, the IFL has an important effect on the photoconductivity of polymer (I). When the thickness of the IFL is about 3 μm, the photoconductivity of polymer (I) is better.

4. Influence of Charge Transport Material on the Photoconductivity of Polymer (I)

Table IV shows the influence of charge transport material (CTM) on the photoconductivity of polymer (I). We can see that the photoconductivity of polymer (I) varies with different kinds and propor-

Table IV Influence of CTM on the Photoconductivity of Polymer (I)

CTM (wt)	R_d (V/s)	R_p (V/s)	$\Delta V_1\%$	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (1/s)
TPD : PVK : PMMA = 5 : 2.5 : 1	22	420	60.6	0.76	1.32
TPD : PVK : PMMA = 5 : 1 : 1	24	371	54.4	0.84	1.19
TPD : PVK : PMMA = 2.5 : 5 : 1	35	305	27.5	2.30	0.43
TPD : TPA : PVK : PMMA = 2.5 : 2.5 : 1 : 1	26	508	37.7	1.61	0.62
TPD : TPA : PVK : PMMA = 2 : 1 : 1 : 1	31	368	40.7	1.30	0.77
TPD : TPA : PVK : PMMA = 1 : 2 : 1 : 1	45	431	31.9	1.69	0.59
TPA : PVK : PMMA = 5 : 1 : 1	10	30	5.8	—	—
TPA : PVK : PMMA = 5 : 2.5 : 1	12	48	4.3	—	—

The thickness of IFL is about 1.2 μm.

tions of CTM. Among TPD–PVK, TPA–PVK, and TPD–TPA–PVK, three transportation compounds, TPD–PVK is the best for polymer (**I**), whereas TPA–PVK is the worst. For CTM of TPD–PVK, when the proportation is TPD : PVK : PMMA = 5 : 2.5 : 1, the photoconductivity of polymer (**I**) is better.

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