ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 88 (1995) 183–186

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Synthesis and photoconductivity study of VK–AA copolymer containing CuPc

Mang Wang, Hong-Zheng Chen, Shi-Lin Yang

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 22 September 1994; accepted 29 November 1994

Abstract

A novel kind of copolymer consisting of poly(vinylcarbazole-co-acrylamide)-bonded $CuPc(NO_2)_2$ was synthesized by the reaction of the diazonium salt of dinitro-diamino copper phthalocyanine with vinylcarbazole and acrylamide. The polymer showed good photoconductivity, much better than that of the corresponding phthalocyanine monomer $CuPc(NO_2)_4$. The main factors influencing the photoconductivity were also studied.

Keywords: Photoconductivity; Phthalocyanine polymer

1. Introduction

Many phthalocyanine polymers have been prepared so far, including one-dimensional phthalocyanine polymers [1,2] and polymer-bonded phthalocyanines [3,4]. However, there have been few studies on their photoconductivity. Recently we obtained a series of polymer-bonded phthalocyanines (Fig. 1) and studied their photoconductivity [5–8]. In this paper we describe the synthesis of a novel copolymer of poly(vinylcarbazole-co-acrylamide)-bonded copper phthalocyanine [P(VK-co-AA)–CuPc] and investigate its photoconductivity.

2. Experimental details

2.1. Materials and equipment

Vinylcarbazole (VK), acrylamide (AA), triphenylamine (TPA) and the other reagents were commercially available and of analytical grade. Polyvinylcarbazole (PVK), *N*,*N*,*N*′,*N*′-tetraphenyl-benzidine (TPD) and pyrazoline (PZL) were synthesized in our laboratory. The diazonium salt of dinitro-diamino copper phthalocyanine was prepared by published procedures [5].

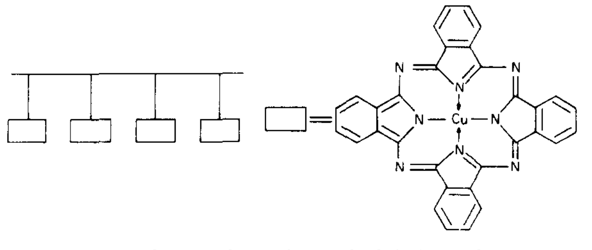


Fig. 1. Structure of the polymer-bonded phthalocyanines.

IR spectra were recorded on an NIC-5DX Fourier transform infrared spectrometer and UV–visible spectra on a DU-50 spectrophotometer. Atomic absorption spectrochemical analysis was performed on a 180-50 atomic absorption spectrophotometer. Photoconductive properties were studied using a model GDT-II photoconductivity-measuring device.

2.2. Synthesis of poly(vinylcarbazole-co-acrylamide)-bonded $CuPc(NO_2)_2$

(a) 7.7 g of VK, 9 g of AA, the diazonium salt aqueous solution of 3.5 g dinitro-diamino phthalocyanine and 0.2 g of dodecyl sodium sulphate were mixed in a 250 ml round-bottomed flask and allowed to stand for 0.5 h at 0–5 °C. Then the reaction mixture was heated to 60 °C for 5 h by hot polymerization. The product was filtered and the solid was washed with water to eliminate PAA and AA, then dried at room temperature in vacuum. The product obtained was added to 50 ml of dimethylformamide (DMF); after filtering, the filtrate was precipitated by ether and the solvent was vaporized. The dark blue crystal I was obtained.

(b) 7.7 g of VK, 9 g of AA, the diazonium salt aqueous solution of 3.5 g dinitro-diamino phthalocyanine and 0.2 g of dodecyl sodium sulphate were mixed in a 250 ml round-bottomed flask and allowed to stand

SSDI 1010-6030(94)04011-7

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 purified by the same processes as in (a) and a dark blue crystal of poly(vinylcarbazole-co-acrylamide)-bonded $CuPc(NO_2)_2$ (**II**) was obtained.

2.3. Preparation of double-layer photoreceptor device and measurement of its photoconductivity [5–8]

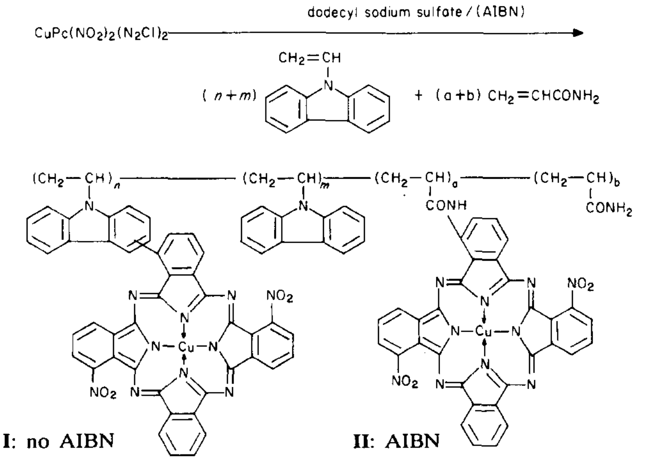
A functional separated double-layer photoreceptor device (P/R) was made by coating an interface layer (IFL) of polymethyl methacrylate (PMMA), a charge generation layer (CGL) of polymer **I** or polymer **II** and a charge transportation layer (CTL) of TPD–PVK, TPA–PVK or PZL–PVK on an aluminium plate in that order.

A model GDT-II photoconductivity-measuring device was used with a 5 W, 24 V visible lamp as 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 hole charge carriers were generated in the CGL and injected into the CTL under exposure. From the PIDC we obtained ΔV_1 (%), which is the percentage of potential discharge after 1 s of exposure, and $t_{1/2}$ (s), which is the time from the original potential to half that value on exposure. The $t_{1/2}^{-1}$ values may be taken as an indicator of photosensitivity. The larger the $t_{1/2}^{-1}$ value, the higher is the photosensitivity of the material.

3. Results and discussion

3.1. Synthesis of poly(vinylcarbazole-co-acrylamide)-bonded $CuPc(NO_2)_2$

Poly(vinylcarbazole-co-acrylamide)-bonded $CuPc(NO_2)_2$ was synthesized by the reaction of the diazonium salt of dinitro-diamino CuPc with VK and AA:



When the mixture reacted by hot polymerization without AIBN, polymer **I** was obtained; when the mixture polymerized by the initiation of AIBN, polymer **II** was obtained. Both purified polymers **I** and **II** are dark blue crystals. They are insoluble in water but soluble in dimethylformamide (DMF) and slightly soluble in tetrahydrofuran (THF), giving blue solutions.

Fig. 2 shows the IR spectra of polymers **I** and **II**. We see that both polymers display absorption bands at 1335, 1170, 1120, 1095, 905, 805 and 750 cm^{-1} which are the typical absorptions of phthalocyanine. They also show a wide absorption band at 1670 cm^{-1} which is the characteristic absorption of PAA. This suggests that both CuPc and PAA structures exist in the two polymers.

From the UV–visible spectra of the two polymers (Fig. 3) we find that polymers **I** and **II** display maximum

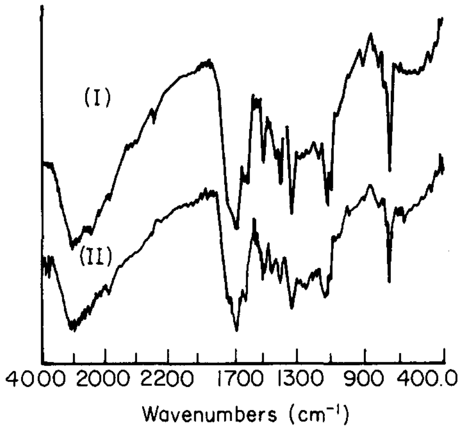


Fig. 2. IR spectra of polymers I and II.

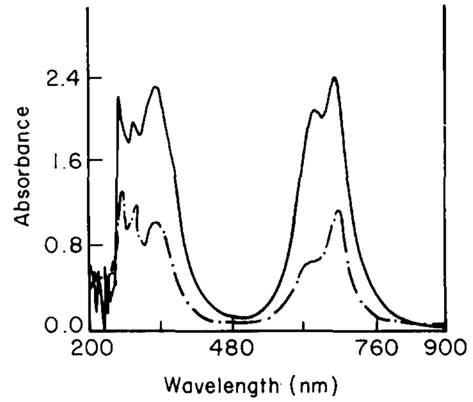


Fig. 3. UV–visible spectra of polymers I (– - –) and II (——). Solvent: DMF.

Table 1
Content of CuPc in the copolymers

Copolymer	Burning method (wt.%)	Atomic absorption (wt.%)	CuPc (wt.%)
I	29.3	29.9	29.6
II	39.1	39.0	39.1

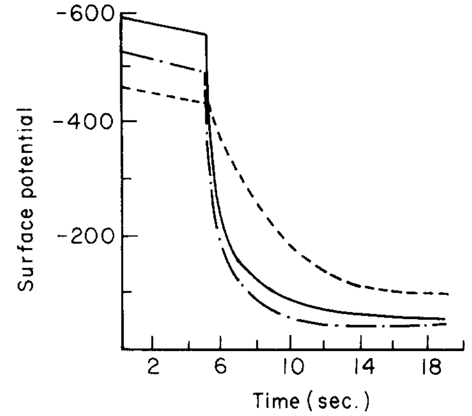


Fig. 4. PIDC of P/R from polymers I (——) and II (–·–) and CuPc$(NO_2)_4$ (– – –). CTM is TPD:PVK:PMMA = 5:2.5:1 (by weight).

peaks at 680 and 682 nm respectively which are due to the existence of phthalocyanine. Furthermore, both polymers **I** and **II** show the typical absorption of PVK in the violet region (200–400 nm). This indicates that both PVK and CuPc structures exist in polymers **I** and **II**.

Thus we may say that polymers **I** and **II** have similar structures of poly(vinylcarbazole-co-acrylamide)-bonded CuPc$(NO_2)_2$.

Table 1 gives the content of CuPc in the polymers. We can see that the weight content of CuPc determined by the burning method agrees with that from the atomic absorption spectrochemical analysis. Polymers **I** and **II** are bonded with 29.6 and 39.1 wt.% CuPc$(NO_2)_2$ respectively.

3.2. Photoconductivity of poly(vinylcarbazole-co-acrylamide)-bonded CuPc$(NO_2)_2$

From Fig. 4 and Table 2 we find that, using charge transport material (CTM) of TPD:PVK:PMMA = 5:2.5:1, polymers **I** and **II** have good charge acceptance (V_0) of 588 and 523 V respectively and low residual potential (V_r) of 76 and 62 V respectively. The surface potentials decrease suddenly at the beginning of exposure. The rates of dark discharge (R_d) are 19 and 25 V s^{-1}, the rates of photodischarge (R_p) are 250 and 312 V s^{-1}, the half-discharge times ($t_{1/2}$) are 0.438 and 0.375 s and the percentages of potential discharge after 1 s of exposure (ΔV_1) are 71.4% and 79.2% respectively. These values indicate that both polymers **I** and **II** have good charge acceptance, small R_d and large R_p, showing good photoconductivity.

From Fig. 4 and Table 2 we also find that, compared with the CuPc$(NO_2)_4$ monomer, polymers **I** and **II** have bigger values of R_p, smaller R_d and shorter $t_{1/2}$, indicating that polymers **I** and **II** have much better photoconductivity than the CuPc$(NO_2)_4$ monomer.

From the structures of polymers **I** and **II** we can see that bigger Π-conjugated systems are formed between CuPc$(NO_2)_2$ and the P(VK-co-AA) main chain, which could enhance the activity of electrons so that they could be excited more easily [5]. Furthermore, there are strong electron acceptor groups ($-NO_2$) on the phthalocyanine rings and also electron donor groups (≡N:) on the same polymer chain P(VK-co-AA). The interaction of the electron acceptor and electron donor groups may help the charge carriers move, hence increasing the photoconductivity [5–7].

3.3. influence of charge transport material on the photoconductivity of polymers I and II

Table 2 reveals the influence of CTM on the photoconductivity of polymers **I** and **II**. We can see that the photoconductivity of polymers **I** and **II** varies with different kinds and proportions of CTM. TPD–PVK is

Table 2
Photoconductivity of the two copolymers and CuPc$(NO_2)_4$

CTM	CGL	V_0 (V)	V_r (V)	R_d (V s^{-1})	R_p (V s^{-1})	ΔV_1 (%)	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
TPD:PVK:PMMA = 5:2.5:1	I	588	76	19	250	71.4	0.438	2.286
	II	523	62	25	312	79.2	0.375	2.667
	CuPc$(NO_2)_4$	463	102	14	108	24.2	4.250	0.235
PZL:PVK:PMMA = 5:2.5:1	I	851	210	–	–	23.0	3.563	0.281
	II	505	74	–	–	46.5	1.108	0.903
PZL:PVK:PMMA = 5:1:1	I	945	195	–	–	28.4	2.250	0.444
	II	1054	226	–	–	26.2	2.625	0.381
PZL:PMMA = 5:1	I	575	144	–	–	46.5	1.188	0.842
	II	431	152	–	–	29.0	2.688	0.372
TPA:PMMA = 1:1	I	524	197	–	–	17.6	7.125	0.140
	II	445	181	–	–	17.4	7.250	0.138
TPA:PMMA = 1:2	I	498	176	–	–	19.9	5.108	0.196
	II	583	297	–	–	10.2	9.125	0.110

Note: the thicknesses of the IFL, CGL and CTL are about 2, 5 and 15 μm respectively.

better than PZL–PVK and TPA–PVK for polymers **I** and **II**, and when its proportion is TPD:PVK:PMMA = 5:2.5:1 (by weight), the ΔV_1 and $t_{1/2}^{-1}$ values reach maxima, showing that the photoconductivity of polymers **I** and **II** is best.

We also studied the influence of thickness on the photoconductivity of polymers **I** and **II**. The results show that when the thickness of the IFL is about 2 μm, the CGL about 1.5 μm and the CTL 10–15 μm, the photoconductivity of polymers **I** and **II** is better.

Acknowledgements

This work was financed by the National Natural Science Foundation of China and also by the Science Foundation of Zhejiang University.

References

[1] K. Fisher and M. Hanack, *Chem. Ber., 116* (1983) 1860.

[2] O. Schneider and M. Hanack, *Chem. Ber., 116* (1983) 2088.

[3] J.H. Schutten and J. Zwart, *J. Mol. Catal., 5* (1979) 109.

[4] J. Zwart and J.H.M.C. Van Wolput, *J. Mol. Catal., 5* (1979) 235.

[5] H.Z. Chen, M. Wang, L.X. Feng and S.L. Yang, *J. Appl. Polym. Sci., 46* (1992) 1033.

[6] H.Z. Chen, M. Wang, L.X. Feng and S.L. Yang, *J. Polym. Sci. A, 31* (1993) 1165.

[7] H.Z. Chen, M. Wang, L.X. Feng and S.L. Yang, *J. Appl. Polym. Sci., 49* (4) (1993) 679.

[8] H.Z. Chen, M. Wang, L.X. Feng and S.L. Yang, *J. Photochem. Photobiol. A: Chem., 70* (1993) 179.