Synthesis and Photoconductivity Study of Phthalocyanine Polymers. VI. Ethylenediamine Bridged Polymeric MnPc

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ABSTRACT: A novel polymer with quasi-one-dimensional structure of ethylenediamine bridged polymeric manganese phthalocyanine $[PcMn(eda)]_n$ was synthesized by complexing of manganese phthalocyanine (MnPc) and ethylenediamine (eda). The structure of the polymer was identified by infrared, ultraviolet–visible, and differential scanning calorimetric analysis. It was found that the polymer $[PcMn(eda)]_n$ showed much better photoconductive property than MnPc monomer when $[PcMn(eda)]_n$ or MnPc was used as the charge-generation material (CGM)-matched hydrazone charge-transportation material (CTM). Furthermore, the photoconductivities of $[PcMn(eda)]_n$ and MnPc were improved if the charge-generation layers (CGLs) were made by electric field poling. All these observations are ascribed to the effects of the one-dimensional molecular structure and the ordered material structure, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2609–2613, 1998

Key words: bridged polymeric phthalocyanine; photoconductivity; one-dimensional structure; electric field poling

INTRODUCTION

Phthalocyanine polymers have received much attention recently because of their potential applications in photovoltaic and xerographic photoreceptors, wherein the kind of one-dimensional conductor through the coordination of phthalocyanine rings (Pc), transition metal atoms (M), and axial bridging ligands (L) to form linear polymeric stacked arrangements $[PcML]_n$ was extensively investigated.[1–9] It was suggested that this polymeric backbone structure with a face-to-face stacked phthalocyanine ring arrangement might give rise to efficient electronic charge transport.[1] On the other hand, the material structure of photoconductive materials, such as different molecular stacking arrangements, conformation of molecules, and particle size, influenced photosensitivity greatly. Our study showed that the photoconductivity of silicon dichloride phthalocyanine ($SiCl_2Pc$) was improved if the charge-generation layer (CGL) containing $SiCl_2Pc$ of the photoreceptor (P/R) was coated in an electric field, which resulted from the orientations of both the molecules and polarity of $SiCl_2Pc$ by the electric field.[10]

In this article, ethylenediamine (eda) monomer was used to coordinate with manganese phthalocyanine (MnPc) to obtain a novel bridged polymeric phthalocyanine $[PcMn(eda)]_n$, which was then polarized by an electric field to give a low-dimensional photoreceptor. Their photoconductive properties were studied as well.

EXPERIMENTAL DETAILS

Materials and Equipment

MnPc was prepared according to the published procedures.[11,12] Ethylenediamine (eda) and the

other reagents were commercially available and of analytical grade. Polyvinylcarbazole (PVK), polycarbonate (PC), poly(methyl methacrylate) (PMMA), polyvinyl butyral (PVB), polyaminoester (PAE), polyvinyl difluoride (PVDF), α-naphthalic hydrazone (NPH), and p-diethylaminobenzaldehyde diphenylhydrazone (DEDPH) were purified by recrystallization.

Infrared (IR) spectra of the samples in KBr pellets were recorded on a NIC-5DX Fourier transform infrared (FTIR) spectrometer. Ultraviolet–visible (UV–VIS) spectra of the samples [$\sim 10^{-3}$ mg/mL in N,N'-dimethylformamide (DMF)] were taken on a DU-50 Spectrophotometer (correcting for DMF absorption). Differential scanning calorimetry (DSC) curves were recorded on a Perkin–Elmer DSC-7 differential scanning calorimeter under N_2, and scanning rate was 20°C/min. Elemental analysis was determined on a Perkin–Elmer 240C elemental analyzer. Photoconductive properties were performed on a GDT-II model photoconductivity measuring device.

Synthesis of [PcMn(eda)]$_n$

0.25 mL (3.68 mmol) of ethylenediamine (eda) and 0.6 g (1.06 mmol) of MnPc were added into 50 mL of DMF solvent. The mixture was stirred with N_2 at 25°C for 13 days. After filtration, the solid was washed with DMF and alcohol to remove the unreacted ethylenediamine monomer completely and dried at 40°C in vacuum, giving a dark blue powder.

ANAL. Calcd for [PcMn(eda)]$_n$ (627n): C, 65.07%; N, 22.33%; H, 3.83%. Found: C, 64.29%; N, 21.91%; H, 3.72%.

Preparation of Double-Layered Photoreceptor Device and Measurement of its Photoconductivity

A double-layered photoreceptor device (P/R) is made by coating the interface layer (IFL), the CGL, and the CTL successively onto a aluminium substrate (see Fig. 1).[13,14] The IFL is PMMA or PAE and $\sim$ 2 μm in thickness. The CGL is $\sim$ 1 μm, and the concentration of [PcMn(eda)]$_n$ or MnPc in the CGL is 11% by weight. The polymer binder for the CGL is the mixture of PVB and PVDF (1 : 1, by weight). The CTL is $\sim$ 30 μm and contains NPH-PC-PVK (4 : 4 : 1, by weight) or DEDPE-PC (1 : 1, by weight). The CGLs are formed two ways: one is by drying at 50°C in an electric field (1×10^4 V/m) for 24 h; the other is by drying at 80°C without an electric field for 1 h.

A GDT-II model photoconductivity measuring device with a visible lamp (5 W, 24 V) as a light source was used to plot the photoinduced discharge curve (PIDC) of the P/R. In this measurement, the surface of the P/R was negatively charged in the dark at first, then the charge carriers were generated in the CGL and injected into the CTL under exposure. From the PIDC, we obtain the percentage of potential discharge after 1 s of exposure (ΔV_1), the time from the original potential to half value on exposure ($t_{1/2}$), and the half-discharge exposure energy ($E_{1/2}$), which equals the product of the exposure intensity I and $t_{1/2}$. All of these three parameters may be taken as an indicator of photosensitivity. The larger the ΔV_1 value, the lower the $t_{1/2}$ and $E_{1/2}$, and the higher the photosensitivity.

RESULTS AND DISCUSSION

Synthesis of [PcMn(eda)]$_n$

Ethylenediamine (eda) is a nucleophile reagent and has a strong coordinating ability, while the group -NH_2 has an isolated electron pair; therefore, it is possible to synthesize [PcMn(eda)]$_n$ by the complexing of eda and MnPc monomers. The complex reaction is followed by
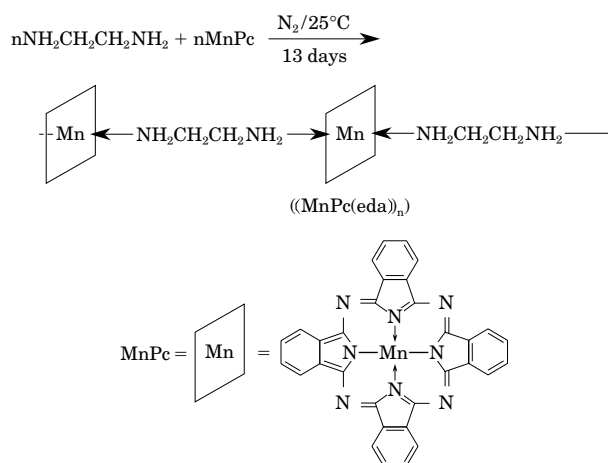

Figure 2 is the IR spectra of [PcMn(eda)]$_n$ and MnPc. The polymer shows absorption bands at 1330, 1080, 900, 750, and 730 cm^{-1}, which are the typical absorptions of phthalocyanine rings. When compared to that of MnPc, the IR spctrum of the polymer shows three new absorption bands at about 2920, 1600, and 1200 cm^{-1}. To assign

Figure 1 Structural scheme of a double-layered photoreceptor (P/R).

these three bands, we subtract MnPc from the $[PcMn(eda)]_n$ spectrum and find a strong resemblance between the subtraction spectrum [Fig. 2(c)] of $[PcMn(eda)]_n$ and MnPc and the standard spectrum of ethylenediamine ($\nu_{N-H} = 3400 \text{ cm}^{-1}$, $\nu_{C-H} = 2920 \text{ cm}^{-1}$, $\delta_{N-H} = 1600 \text{ cm}^{-1}$, and $\nu_{C-N} = 1200 \text{ cm}^{-1}$), which indicates that ethylenediamine has complexed with MnPc.

From the UV–VIS spectra of the polymer and MnPc (Fig. 3), we find that the polymer has the typical absorptions of phthalocyanine rings (706, 620, and 330 nm), which are weaker than that of MnPc. We also notice that the polymer shows no absorption at 495 nm, where the MnPc monomer shows. According to the study of Engelsma et al.,[15] the absorption at 495 nm of MnPc belongs to MLCT band (charge transition shift band), which may result from partial charge transfer from phthalocyanine ring to Mn atom ($Pc^{\delta+} \rightarrow Mn^{\delta-}$) in MnPc molecules.[16] It suggests that the coordi-
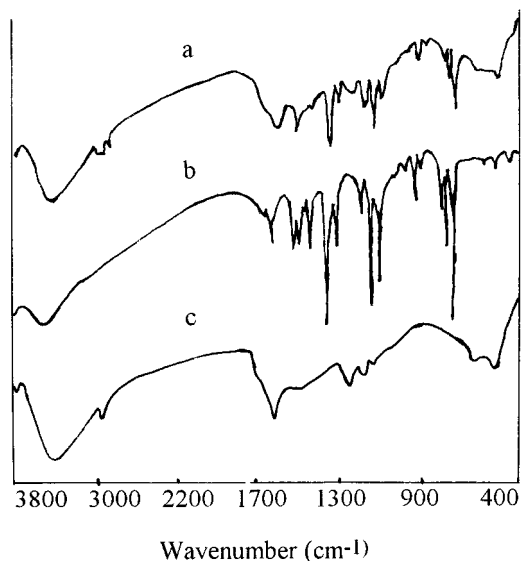

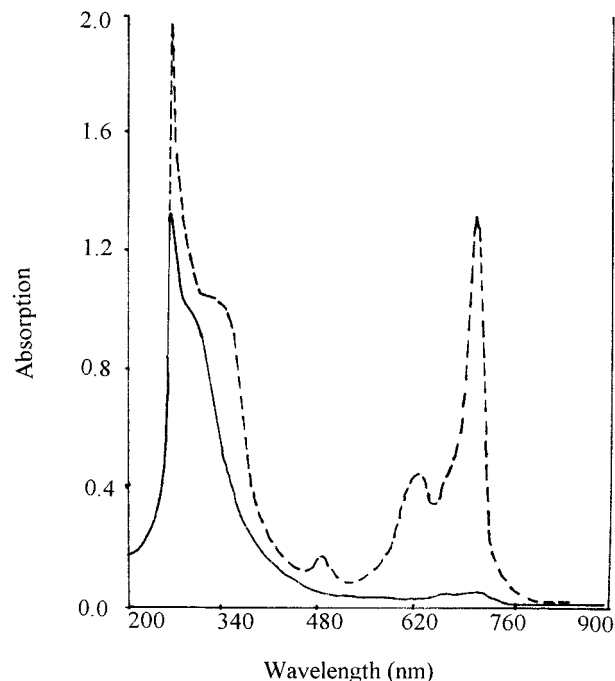**Figure 2** IR spectra of (a) $[PcMn(eda)]_n$ (b) MnPc, and (c) subtraction of $[PcMn(eda)]_n$–MnPc in KBr pellets.

Figure 3 UV–VIS spectra of $[PcMn(eda)]_n$ (——) and MnPc (- - - - -) ($\sim 10^{-3}$ mg/mL in DMF).

nation of an $-NH_2$ and Mn atom prevents the charge transfer from the Pc ring to the Mn atom and leads to no absorption at 495 nm in the UV–VIS spectrum of the polymer.

From the DSC curves of $[PcMn(eda)]_n$ and MnPc (Fig. 4), we find that the DSC curve of MnPc is almost a line, while the DSC curve of $[PcMn(eda)]_n$ has a peak at about 240°C. It suggests that at about 240°C, $[PcMn(eda)]_n$ gives out of the ethylenediamine monomer. All of the above observations indicate that eda and MnPc monomers must have coordinated each other, and eda-bridged MnPc polymer with quasi-one-dimensional molecular structure is obtained. However, the polymeric degree of the polymer is difficult to determine because of its poor solubility.

Photoconductivities of $[PcMn(eda)]_n$ and MnPc

Table I shows the photoconductivities of the P/Rs from $[PcMn(eda)]_n$ and MnPc. We can see that when PMMA is used as interface material (IFM) and NPH-PC-PVK is used as CTM, $[PcMn(eda)]_n$ has good charge acceptance ($V_0 = 527$ V), a small rate of dark discharge ($Rd = 11$ V/s), a fast rate of photo discharge ($R_p = 125$ V/s). The percentage of potential discharge after 1 s of exposure ($\Delta V_1\%$) is 79.3%, the time of
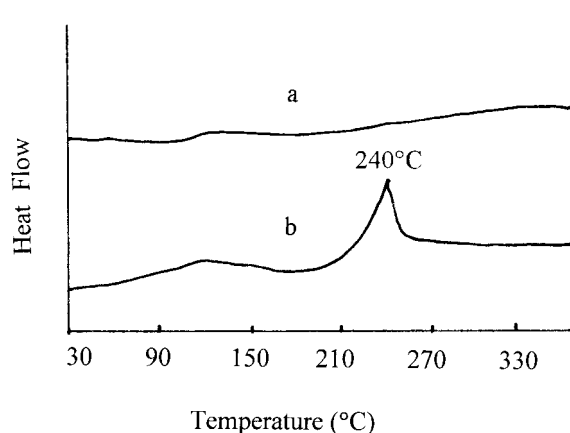
Figure 4 DSC curves of (a) MnPc and (b) [Pc-Mn(eda)]$_n$.

half-discharge ($t_{1/2}$) is 0.25 s, and the half-discharge exposure energy ($E_{1/2}$) is 200 lux · s, indicating good photoconductivity. Compared with that of MnPc, we can see that the V_0 and $\Delta V_1\%$ values of MnPc are smaller, while $t_{1/2}$ and $E_{1/2}$ values are larger than those of [PcMn(eda)]$_n$, suggesting that [PcMn(eda)]$_n$ has better photoconductivity than MnPc. If polyaminoester (PAE) is used as IFM instead of PMMA, the same conclusion could be drawn.

The differences of the photoconductivity of [PcMn(eda)]$_n$ and MnPc may result from their structures. To the polymer [PcMn(eda)]$_n$, its molecule belongs to a one-dimensional structure[1,4-6,9] where phthalocyanine rings range in face-to-face and an axial electron passage is formed,[4] which is benefit to charge carriers orienting migration. On the other hand, the coordination may bring about change of the coordination field of Mn atom from octahedron field to tetrahedron field, leading to recombination of molecular orbit energy level, which is helpful to reduce the energy of charge carriers transition

and, hence, improve the charge carriers migration.

Effect of Electric Field Poling on Photoconductivities of [PcMn(eda)]$_n$ and MnPc

Table II compares the photoconductivities of P/Rs from [PcMn(eda)]$_n$ and MnPc when CGLs are made in an electric field with that when CGLs are coated without an electric field. To [PcMn(eda)]$_n$, when PMMA is used as IFM and NPH-PC-PVK (4 : 4 : 1, by weight) is used as CTM, the $E_{1/2}$ value decreases to 200 from 350 lux · s, while ΔV_1 increases to 80.0% from 67.2% if an electric field is applied, indicating that [PcMn(ead)]$_n$ has better photoconductivity after electric field poling. If PAE takes the place of PMMA as IFM, the same conclusion could be drawn as well. To MnPc, we may also find that photoconductivity of MnPc increases if an electric field is used.

The above experimental results may be explained in the view of material structure. It is well known that PVDF is a molecule with a permanent dipole moment due to its 2 fluorine atoms, which makes the molecules and dipole moment of PVDF easy to orientate in an electric field. When coating CGLs of [PcMn(eda)]$_n$—PVB—PVDF or MnPc—PVB—PVDF in an electric field ($E = 1 \times 10^4$ V/m), the molecules and dipole moment of PVDF orientate along the electric field direction. The orientation of PVDF may induce an electrical polarity of [PcMn(eda)]$_n$ or MnPc dispersed in PVDF and make both the molecules and dipole moment of [PcMn(eda)]$_n$ or MnPc also orientate. Our recent studies of DSC, angle-dependent X-ray photoelectron spectroscopy, and FTIR reflection absorption spectroscopy provide strong support for the molecular preferential alignment poled by an electric field in [PcFe(eda)]$_n$.[17] It is the ordered material structure that is favorable to the charge carriers migration, and the photoconductivities therefore increase.

Table I   Photoconductivities of P/Rs from [PcMn(eda)]$_n$ and MnPc

CGM	IFM	V_0 (V)	R_d (V/s)	R_p (V/s)	ΔV_1 (%)	$t_{1/2}$ (s)	$E_{1/2}$ (lux · s)
[PcMn(eda)]$_n$: PVB : PVDF = 1 : 4 : 4 (by wt)	PMMA	527	11	125	79.3	0.25	200
	PAE	562	41	187	81.3	0.25	200
MnPc : PVB : PVDF = 1 : 4 : 4 (by wt)	PMMA	265	15	93	60.7	0.56	448
	PAE	289	16	93	58.1	0.63	504

CTM is NPH : PC : PVK = 4 : 4 : 1 (by wt). Exposure intensity was 800 lux. The thicknesses of IFL, CGL, and CTL are about 2, 1, and 30 μm, respectively. CGL is formed rapidly at 80°C for 1 h.

Table II   Effect of Electric Field Poling on Photoconductivities of P/Rs from [PcMn(eda)]$_n$ and MnPc

CGM	CTM	IFM	E $(10^4$ V/m)	R_d (V/s)	R_p (V/s)	ΔV_1 (%)	$t_{1/2}$ (s)	$E_{1/2}$ (lux · s)
MnPc : PVB : PVDF	a	PMMA	0	10	125	43.4	1.31	1050
= 1 : 4 : 4 (by wt)			1	10	156	46.4	1.13	800
[PcMn(eda)]$_n$: PVB : PVDF	b	PMMA	0	12	62	67.2	0.44	350
= 1 : 4 : 4 (by wt)			1	19	125	80.0	0.25	200
		PAE	0	19	125	73.1	0.38	300
			1	23	162	79.6	0.25	200

a, DEDPH–PC (1 : 1, by wt); b, NPH–PC–PVK (4 : 4 : 1, by wt). Exposure intensity was 800 lux; the thicknesses of IFL, CGL, and CTL are about 2, 1, and 30 μm, respectively. CGL is formed slowly at 50°C for 24 h.

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