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PHOTOINDUCED CHARGE SEPARATION OF POLYSTYRENE- BOUND Ni(II)-4,4'-4'', 4'''-TETRACARBOXYPHTHALOCYANINE

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ABSTRACT

Polystyrene with pendant Ni(II)-4,4',4'',4'''-tetracarboxyphthalocyanine (NiPtc) was synthesized by reacting NiPtc with partially chloromethylated polystyrene. Photoreduction of methylviologen by visible light was accomplished with the modified polymer. The photocatalytic activity was enhanced by bonding the NiPtc units to the polymer. The relationship between the catalytic activity and the structure of the modified polymer is discussed.

INTRODUCTION

Phthalocyanines are industrially important pigments and are used in a wide range of products, including plastics, coatings, paints, and inks. As they are chemically stable and have redox activity and strong extinction coefficients over a range of the visible spectrum, we have paid attention to their characterization and catalytic activity. We reported electrochemical reduction of carbon monoxide, formic acid, and formaldehyde on a glassy carbon electrode modified by Co(II)-4,4',4'',4'''-tetracarboxyphthalocyanine [1].

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Recently metallophthalocyanines have been considered as catalysts for the chemical conversion of solar energy. Tanno [2], Maillard [3], Harriman [4], Lever [5], and their coworkers reported separately the photoinduced reduction of methylviologen (MV^{2+}) with metallophthalocyanines and their derivatives as photosensitizers.

Metallophthalocyanines have very attractive photocatalytic activities, but only a few investigators have become involved in this field because of the notorious insolubility of these compounds. One of the best ways to improve the solubility of the phthalocyanine is to bind it to a polymer. In addition, this strategy gives us a tailor-made reaction field that may be more effective for the photoreduction of MV^{2+} .

From this point of view, we have been studying the synthesis of polymers with pendant metallophthalocyanine derivatives and photoinduced charge separation. In our previous paper [6], water-soluble polystyrene with pendant metal-4,4',4'',4'''-tetracarboxyphthalocyanine (metal-Poly-1) was synthesized, and the photoreduction of MV^{2+} was carried out by visible light. We reported metal-Poly-1 (Ni and Cu) had catalytic activity for photoreduction in aqueous solution and discussed the relationship between the catalytic activity and the polymer structure. In this paper we report the synthesis of DMSO-soluble polystyrene-bound Ni-4,4',4'',4'''-tetracarboxyphthalocyanine (Ni-Poly-2) and the photoreduction of MV^{2+} with it and compared the catalytic activity of Poly-2 with that of Poly-1.

EXPERIMENTAL

Materials

Solvents were purified by the usual methods. Trimeric anhydride was purified by recrystallization from acetone. Anhydrous nickel(II) chloride, urea, and ammonium paramolybdate were commercially available and used without further purification. Partially chloromethylated polystyrene (14.3 wt% Cl) was synthesized from polystyrene ($\bar{P}_n = 1\ 700$) and chloromethyl methyl ether. MV^{2+} and triethanolamine (TEOA) were commercially available grades used without further purification.

Ni(II)-4,4',4'',4'''-tetracarboxyphthalocyanine (NiPctc) was synthesized by hydrolysis of Ni(II)-4,4',4'',4'''-tetracarboxyamidophthalocyanine by the method reported by Shirai et al. [7] and purified by the procedure described in our earlier paper [1].

Poly-2 was synthesized by the following procedure. To a dimethylsulfoxide (DMSO) solution of partially chloromethylated polystyrene were added a

DMSO solution of NiPctc and NaHCO_3 . After the solution was heated at 80–90°C for 18 h, it was concentrated under vacuum and poured into distilled water to obtain the modified polymer. The polymer was dissolved in DMSO, and the solution was filtered and poured into distilled water. The reprecipitation was repeated several times until the filtrate was no longer colored. The polymer is soluble in DMSO and DMF. The content of NiPc units in Poly-2 was determined by atomic absorption analysis. The content of NiPc units was 0.042 and 0.017 mmol/g polymer.

Photoreduction

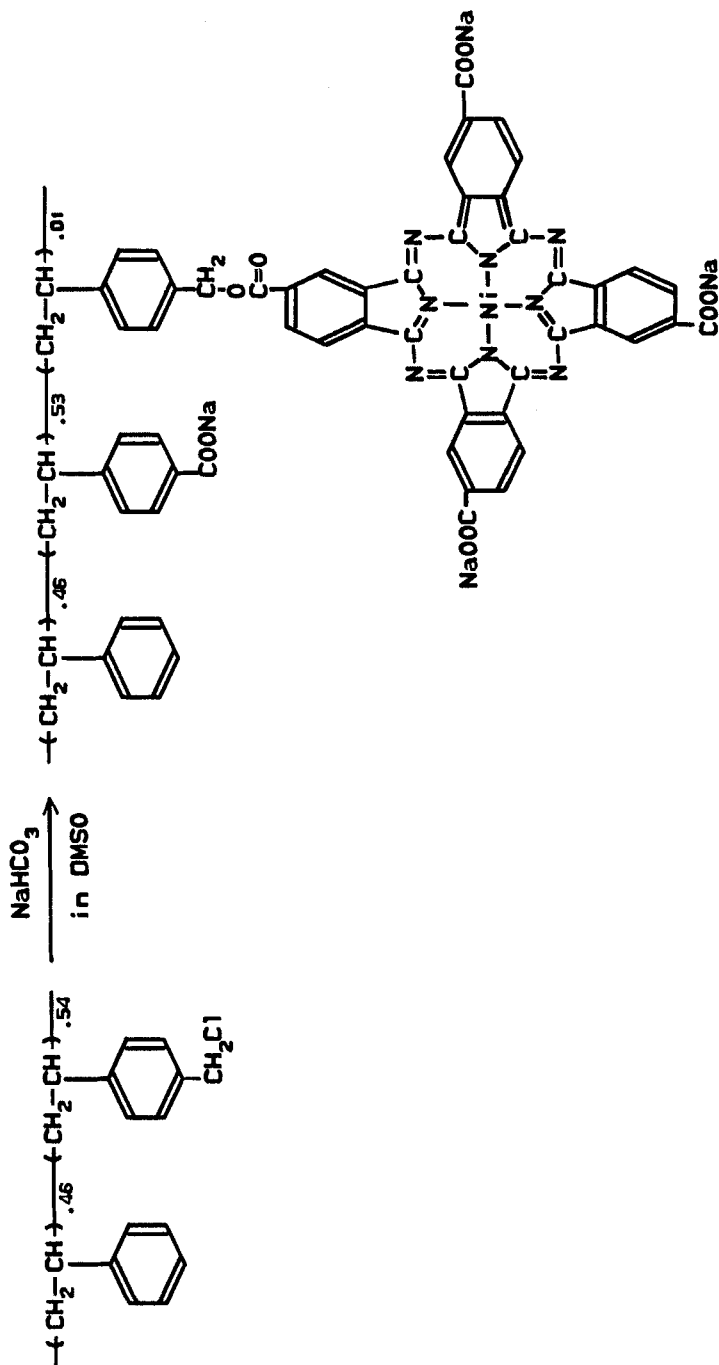
Into a glass ampule with a UV cell were placed a DMSO/ H_2O solution of Poly-2, MV^{2+} , and TEOA. The ampule was flushed with Ar gas for 30 min, degassed, and sealed. Visible light irradiation employed a 500-W xenon lamp in conjunction with a UV and an IR cut-off filters (Toshiba IRP-60 and VY-42). The photoreduction was carried out at 25°C.

Measurements

Visible absorption spectra were measured on a Hitachi Model 200-10 spectrophotometer. Atomic absorption analysis was carried out on Seikou Model SAS-727 spectrophotometer.

RESULTS AND DISCUSSION

The synthesis of polystyrene with pendant NiPctc (Poly-2) was accomplished by reacting NiPctc with partially chloromethylated polystyrene in DMSO. Poly-2 had the intense blue color characteristic of NiPctc and is soluble in DMSO and DMF. Figure 1 shows the visible absorption spectra of Poly-2 and NiPctc in DMSO. NiPctc has two peaks, at 610 and 680 nm, which are assigned to dimeric and monomeric phthalocyanine units, respectively [8–10], while the monomeric and dimeric peaks of Poly-2 are at 690 and 650 nm. The ratio of the monomeric to dimeric peak for poly-NiPctc is greater than that of NiPctc, which suggests that the content of monomeric phthalocyanine units of Poly-2 is higher than that of NiPctc and that the bulkiness of the polymer chain hinders aggregation of NiPctc units in the polymer chain. A similar result was observed for Poly-1 [6]. Shirai et al. [8] synthesized polystyrene-bound Fe(III) and Co(II)-Pctc and reported that aggregation of metal-Pctc units on the polystyrene became more difficult because of the steric hindrance of the polymer chain.



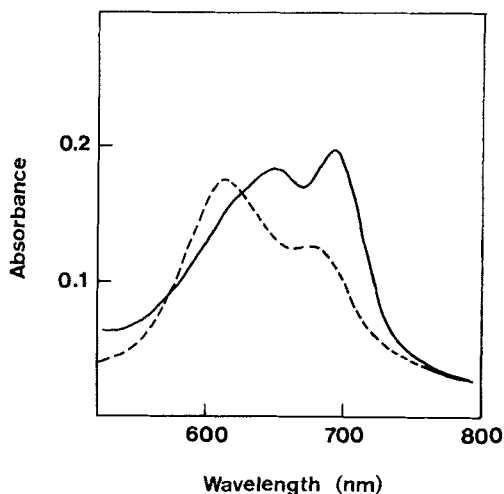


FIG. 1. Visible spectra of NiPtc (---) and Ni-Poly-2 (—, NiPtc units: 0.042 mmol/g polymer) in DMSO. Concentration of NiPtc units: 0.010 mmol/l.

Photoreduction of MV^{2+} with Poly-2 was carried out in UV cell by visible light. TEOA was used as electron donor. Poly-2 and NiPtc exhibited photocatalytic activity for the reduction of MV^{2+} to $MV^{+\bullet}$. The photoreduction of MV^{2+} was monitored by the increase of absorbances at 610 nm due to $MV^{+\bullet}$. The formation of $MV^{+\bullet}$ was confirmed by the differential visible spectrum between the reaction solution before and after irradiation (Fig. 2).

As shown in Table 1, the initial rate of $MV^{+\bullet}$ formation with Poly-2 (Run 5) was about 3 times that with NiPtc (Run 3). The increase in the monomeric units of Ni-Poly-2 compared with NiPtc, described above, may be one of the reasons why the rate of photoreduction with Ni-Poly-2 was faster than that of NiPtc. The result suggests that reversal of $MV^{+\bullet}$ formation is not affected by the negative charges ($-COO^-$ groups) on the lateral chain of Poly-2. Poly-2 with a higher NiPtc content (Run 5) gave higher photocatalytic activity than the polymer with a lower one (Run 7). These results suggest that the increase in the phthalocyanine content in the polymer sequence causes a rise in their local concentration in the reaction solution and thus enhances the photoactivity. The initial rate of $MV^{+\bullet}$ formation in DMSO/ H_2O (96:4, Run 5) is higher than that in DMSO (Run 6). It is thought that the reduction rate decreases with decreasing H_2O content because of the lower

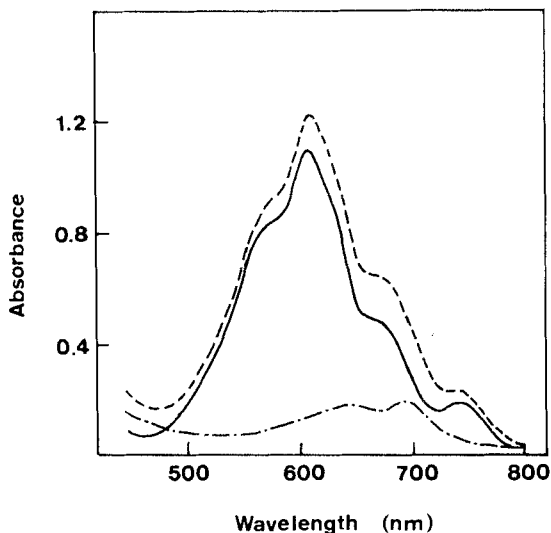


FIG. 2. Visible spectra of $MV^{\bullet+}$ formed (—) and the reaction mixture before (—•) and after (---) irradiation. Concentration of NiPc units: 0.010 mmol/L in DMSO/ H_2O 96:4.

solubility of MV^{2+} in DMSO (Run 6). Tanno et al. reported a similar phenomenon observed for the photoreduction of MV^{2+} with MgPc [2]. In the case of photoreduction in DMSO: H_2O 80:20, Poly-2 was aggregated during photoirradiation and the photoreduction did not occur (Run 4).

We previously synthesized water-soluble polystyrene with pendant metal-Pctc (Poly-1; metal: Ni, Co, and Cu) [5]. Ni- and Cu-Poly-1, with R_4N^+ - and Pc groups on the polymer lateral chain, displayed catalytic activity for the photoreduction of MV^{2+} . The initial rate of photoreduction with Poly-1 (Run 8) was lower than that with Poly-2 (Run 5). As Poly-1 has R_4N^+ groups on the lateral chain, Coulombic repulsions between the positive charges of the R_4N^+ -groups and MV^{2+} might be disadvantageous for photoinduced charge separation. In contrast, Poly-2 has $-COO^-$ groups on the lateral chain, and the attack of MV^{2+} at the photoactivated Pc units was enhanced.

TABLE 1. Photoreduction of MV^{2+} by Visible Light with Polystyrene-Bound Ni(II)-4,4',4'',4'''-Tetracarboxy-phthalocyanine^a

Run ^b	Sensitizer		Reducing agent		Solvent, DMSO:H ₂ O	Initial rate of MV^{2+} formation, $\mu\text{mol}/(\text{L}\cdot\text{min})$	Ref.	
	Type	Concentration, mmol/g polymer	Type	Concentration, mmol/L				
1	MgPc	—	EDTA	12.5	2.5	75:25	6.9	2
2	NiPc	—	EDTA	12.5	2.5	75:25	0.44	2
3	NiPetc	—	TEDA	1.0	0.50	94:4	0.65	c
4	Ni-Poly-2	0.042	TEDA	1.0	0.50	80:20	—	c
5	Ni-Poly-2	0.042	TEDA	1.0	0.50	96:4	2.1	c
6	Ni-Polu-2	0.042	TEDA	1.0	0.50	100:0	1.7	c
7	Ni-Poly-2	0.017	TEDA	1.0	0.50	96:4	1.4	c
8	Ni-Poly-1	0.068	TEDA	1.0	0.50	0:100	0.35	6
9	Ni-Poly-1	0.043	TEDA	1.0	0.50	0:100	0.31	6

^aIn DMSO at 25°C.^bConcentration of metal-Petc units in the reaction mixture: Runs 1-2, 100 $\mu\text{mol}/\text{L}$; Runs 3-9, 10 $\mu\text{mol}/\text{L}$.^cThis work.

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