Photovoltaic and Catalytic Activity of Plasma-Polymerized Phthalocyanine Films

Yoshihito Osada[a]; Akira Mizumoto[a]; Hiroaki Tsuruta[a]

[a] Department of Chemistry, Ibaraki University, Mito, Japan

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PHOTOVOLTAIC AND CATALYTIC ACTIVITY OF PLASMA-POLYMERIZED PHTHALOCYANINE FILMS

YOSHIHITO OSADA,* AKIRA MIZUMOTO, and HIROAKI TSURUTA

Department of Chemistry
Ibaraki University
Mito 310, Japan

ABSTRACT

Polymeric metal (Cu, Mg, Zn, and Ni) and metal-free phthalocyanine thin films were prepared from the gas phase by low-temperature plasma polymerization. Electronic and FT-IR spectra indicated that no extensive alteration or destruction of the original ring structure had occurred. The obtained film showed good rectification, photovoltaic, and electrochromic effects. The film also reduced methyl viologen under visible light, and its catalytic activity was as high as that of monomeric phthalocyanine particles. The formation mechanism and properties of the polymeric phthalocyanine films are discussed briefly.

INTRODUCTION

There is considerable activity in the study of the electronic behavior of organic thin films. Such organic pigments as merocyanine dye [1, 2] have been attracting much attention in recent years. Phthalocyanine is one of the candidate photoactive materials due to its high absorption in the visible region and its chemical stability, and some metal phthalocyanine compounds have been investigated extensively [3, 4]. Phthalocyanine thin films are usually prepared

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*To whom correspondence should be addressed.

either by vacuum deposition [5-10], binding covalently to a polymer chain [11], or dispersing fine particles of pigment in a polymer binder [12-15]. Recently the Langmuir-Blodgett (LB) method has also been examined by using phthalocyanines with attached chains [16]. However, each of these methods appears to suffer from some disadvantage. Thin films prepared by vacuum deposition or the LB method lack mechanical toughness, and it is difficult to prepare films thinner than 100 nm by the other, i.e., casting, methods because of the presence of pinholes. Thus, it seemed appropriate to prepare films that have mechanical toughness as well as submicrometer thickness from macromolecular phthalocyanines.

We succeeded in making such films directly and rapidly by low-temperature plasma polymerization. This is a superior technique for forming thin polymer films from almost all organic vapors [17-20]. Plasma-polymerized films are generally different from the corresponding polymers obtained by conventional methods, in that they are chemically inert, insoluble, and mechanically hard. These characteristics are recognized as arising from chemical reaction such as branching, crosslinking, or destruction of some part of the monomer structure.

In this paper we report the preparation and properties of polymeric phthalocyanine thin films, mainly of copper phthalocyanine (CuPc), prepared by low-temperature plasma polymerization.

EXPERIMENTAL

Plasma Polymerization

The apparatus for plasma polymerization consists of a Pyrex glass bell jar and a pair of parallel electrodes (70 mm diameter) connected to an RFG-200 radio-frequency generator (Samco International Inc.) operating at 13.56 MHz. Polymerization was carried out by evaporating solid CuPc at elevated temperature. For this purpose a heating appliance was mounted in the reactor between the electrodes. CuPc was heated in two ways. One is indirect heating with the radiant heat emitted from a tungsten filament (Method A); the other is the direct evaporation from a tantalum boat (Method B). The optimum conditions for obtaining even and smooth deposition are as follows: pressure 13 Pa (0.1 torr), electrode distance 40 mm, temperature of CuPc evaporation 350-450°C. The substrate (glass plate electrode: ITO glass, 10 ohms per square, 10 × 20 mm) was placed on the lower side of the top electrode, and the plasma was generated for about 60 s. During this time the CuPc was completely evaporated and the substrate was coated with a polymer layer.

Characteristics

All electronic, dark and photo current-voltage (J-V) characteristics, and electrochemical properties were measured by an electrometer (HA-501, Hokutodenko Co.), and recorded on an x-y recorder. The J-V characteristics were measured with sandwich cells consisting of semitransparent Al electrode/plasma-polymerized CuPc/ITO. The Al electrode, which has 8-10% transmittance, was deposited by vacuum evaporation under 1.3 mPa (10^{-5} torr). Photo J-V characteristics were examined by irradiating with the light of a 750-W tungsten lamp through an IR cut-off filter (IRA-25S, Toshiba Co.) from a distance of 25 cm. The light intensity was 100 mW/cm^2, which is almost the same as that of solar energy in the daytime. The power conversion efficiencies of the photovoltaic cells were calculated according to

$$\eta \ (\%) = (J_{sc} V_{oc}/I_t)FF \times 100, \tag{1}$$

where V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit photocurrent, FF is the fill factor, and I_t is the intensity of the light transmitted though the Al electrode.

Cyclic voltammetry was performed in 1.0 M NaClO$_4$ aqueous solution by using a triangular-wave generator (HB-104, Hokuto Co.) with the following electrodes: a Hg/HgCl reference, a Pt auxiliary, and a CuPc-coated ITO working electrode with a scan rate of 100 mV/s.

The surface conditions of the films was observed by SEM (MSM-4C, Akashi Ltd.) and a Taly-step monitor instrument (Dektak II-A, Soloan Co.) with a 10-mg load. The film thickness was measured by SEM, Taly-step, or multibeam interferometry (Model 2, Mizojiri Kogaku Co.). The electronic spectra were measured with a Hitachi spectrophotometer 124. Infrared spectra were obtained by using a FT-IR spectrometer (JEOL JIR-40).

Photoreduction of methyl viologen (MV^{2+}) was performed in mixed H$_2$O/DMSO solution containing 0.5 mM MV^{2+} and 1 mM EDTA as electron donor in a 25-mL Kjeldahl flask. A glass plate on which plasma-polymerized CuPc film was deposited was immersed in the solution. The catalysis of monomeric CuPc was also examined by dispersing its particles in solution at the same weight concentration as the plasma-polymerized CuPc film used by ultrasonics and stirring. The solution (10 mL) was degassed in vacuo and then irradiated by a 120- or 750-W tungsten lamp through an IR cut-off filter from 15 cm distance. The photoreduction was followed by measuring the increase in absorbance at 610 nm due to the reduced concentration of MV$^{\cdot+}$.

Materials

Purified CuPc and metal-free phthalocyanine were kindly provided by Toyo Ink Co. The other phthalocyanine complexes zinc, magnesium, and nickel, were purchased from Kanto Chemical Co. Methyl viologen dichloride was purchased from Tokyo Kasei Co. EDTA was purchased from Kanto Chemical Co. Nickel phthalocyanine was used after purification in vacuum. The other materials were used without further purification.

ITO and glass plate were cleaned by treatment with ultrasonics.

RESULTS AND DISCUSSION

Film Preparation

The plasma-polymerized CuPc(pp-CuPc) obtained was a glossy, greenish thin film 600-8000 Å thick, while CuPc is, as is well known, a deep blue pigment. The polymeric film was smooth and even, as shown in Fig. 1, and was
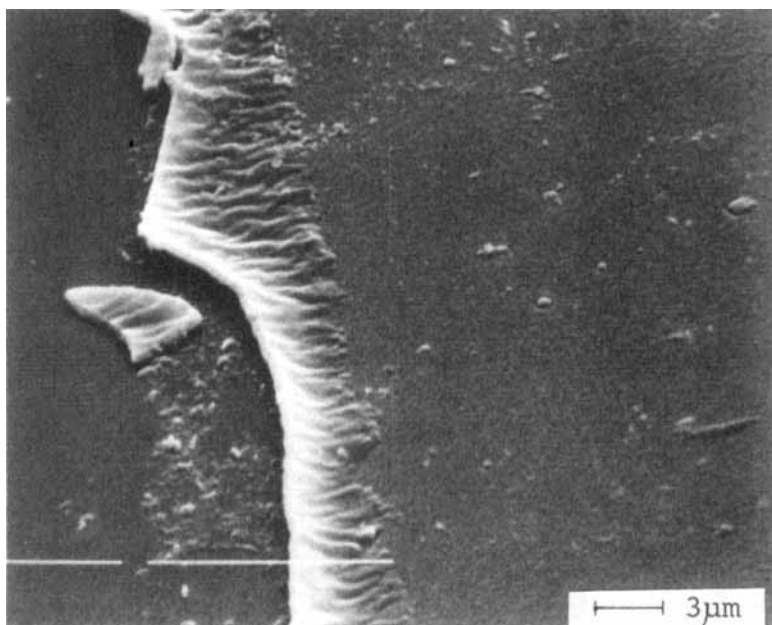

FIG. 1. Scanning electron micrograph of plasma-polymerized CuPc film deposited on glass plate. Wrinkles at the edge of the film were caused when adhesive tape used as a mask was peeled off.
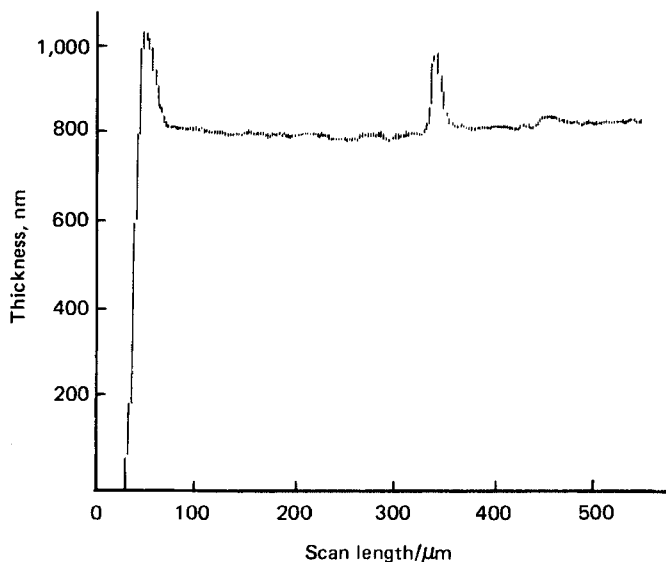
FIG. 2. Thickness and surface profiles of plasma-polymerized CuPc film. A peak at the edge of the film was caused by adhesive tape, as described in Fig. 1. The peak in the middle of the film is due to contamination.

neither soluble in pyridine nor in concentrated sulfuric acid, both of which are good solvents for monomeric CuPc. Figure 2 shows quantitatively that the pp-CuPc film obtained is very smooth and even with a roughness of ±3% or less. In contrast, the film obtained by vacuum evaporation under the same condition, but without the plasma, was easily scratched by the needle of the apparatus, and the thickness measurement by the Taly-step method failed. Mechanically tough and even polymeric film was found only at the lower side of the top electrode of the glow discharge, and the films formed on other surfaces were soluble and easily scratched by the Taly-step measurement. Plasma polymerization of CuPc with a low-frequency generator (90 kHz) failed to yield any polymer.

Figure 3 shows the spectral changes that occur upon plasma polymerization. The spectrum of vacuum deposited film is similar to that of α-phase CuPc crystal [21, 22]. Practically no change was observed in the Soret band (320 nm) upon polymerization. However, the relative intensity in the region of the peaks between 550 and 700 nm was altered, and the splitting between them weakened and decreased. These peaks are known as "Davydov splitting"
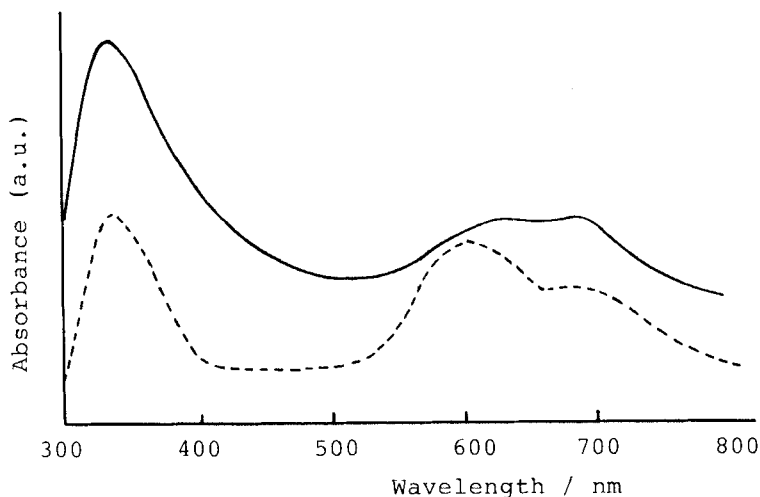
FIG. 3. Electronic spectra of plasma-polymerized (solid curve) and vacuum-deposited (dashed curve) CuPc film. Spectra are displaced vertically for clarity.

[23] and show the presence of interactions between adjacent phthalocyanine molecules. The spectrum in Fig. 3 implies weakened interactions between, or increased spacing of, phthalocyanine molecules in the polymer compared to that of evaporated film.

The FT-IR spectra in Fig. 4 show that most of the absorptions of CuPc also appear in the spectrum of pp-CuPc film, but a new absorption (at $1\ 720\ cm^{-1}$) in pp-CuPc film indicates partial oxidation of the phthalocyanine. At present we cannot illustrate the exact chemical structure of the polymeric phthalocyanine film. However, the film obtained was capable of reducing solvated viologens under visible light and also exhibited the photovoltaic effect and electrochromism, as will be mentioned below. These observations indicate that no extensive alteration or partial damage of the phthalocyanine ring structure occurred.

Electronic Properties

The current through a sandwich in which a 100-nm pp-CuPc layer was interposed between Al and ITO electrodes as a function of applied voltage (dark J-V curve) is shown in Fig. 5. The cell showed rectifying behavior with for-
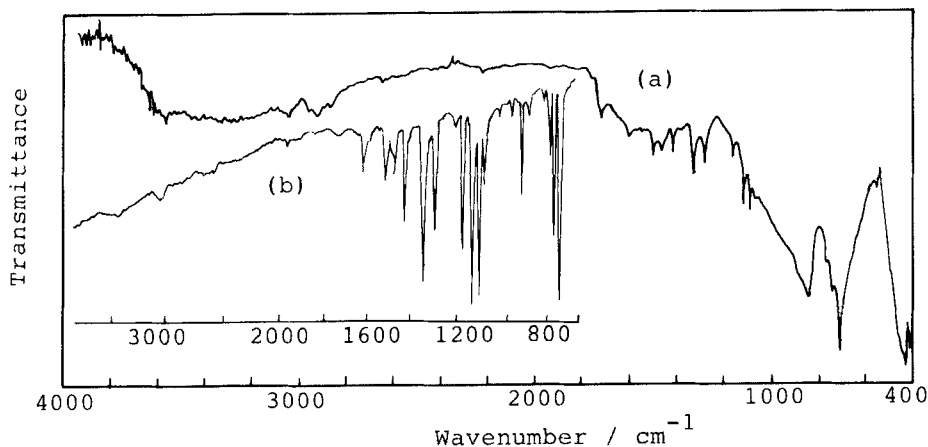
FIG. 4. FT-IR spectra of plasma-polymerized and vacuum-evaporated CuPc films. (a) Plasma-polymerized, (b) Vacuum-evaporated.

ward bias, corresponding to a negative voltage at Al with respect to ITO. The rectifying ratio at 2.0 V was ~20. This behavior is essentially the same as that previously reported for CuPc photovoltaic cells [24, 25]. It is thought that a Schottky barrier formed in the Al/pp-CuPc/ITO sandwich is the origin of the rectification.

From the data in Fig. 5, it was deduced that the forward bias current density, $\ln J$, is proportional to $V^{1/2}$ over the range 0.6 to 2.0 V (Fig. 6). This kind of behavior is characteristic of either Pool-Frenkel emission or of Schottky emission [9]. Since equivalent behavior was not observed when ITO was used for the top contact, it is assumed that current flow in the cell is governed by Schottky emission at the Al/pp-CuPc interface. As Al has a lower work function than ITO, the Schottky barrier height at an Al contact should be higher than at ITO [26]. Figure 5 is also shows the J-V relationship for a pp-CuPc film (Curve B) in which iodine was doped simultaneously with polymerization (simultaneous doping of plasma polymerization) [27]. It is seen that the current increased about 3-5 times and a much higher rectification ratio (about 50) was observed at 2.0 V. We also examined the doping of iodine molecules to pp-CuPc film by the conventional method, i.e., exposing the film to iodine vapor, and no effect of the doping was observed. This should be associated with the density of the film, characteristic of plasma polymerization, so that no diffusion or permeation of iodine vapor into the film occurred.
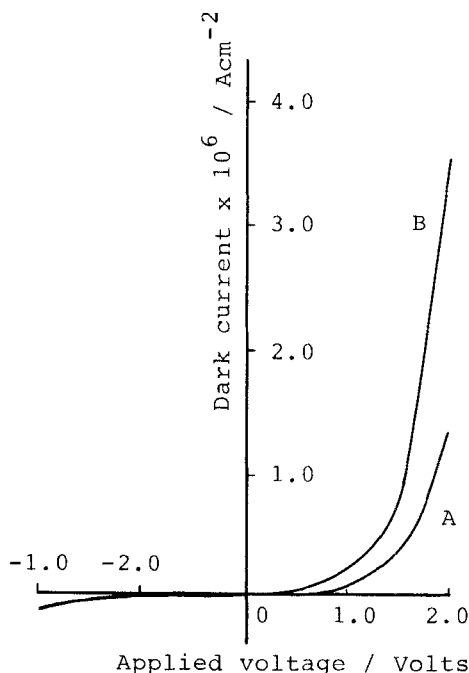
FIG. 5. Dark current-voltage characteristics. (A) Al/plasma-polymerized CuPc film/ITO cell. (B) Al/iodine-doped plasma-polymerized CuPc film/ITO cell. Film thickness, 100 nm.

The CuPc film made by vacuum deposition under the same condition as the plasma polymerization but without plasma generation showed short-circuiting only on imposing 0.5 V and more, and no rectification or even insulation was observed. Rectification by this film was observed only when it was thicker than 400 nm. This should be explained mainly by the differences in the fundamental growth processes involved. Films formed by vacuum deposition should grow according to Volmer-Weber type growth, which is a process of nucleation: "island" growth, eventual coalescence of island, and finally filling-in of voids to form a continuous film as more material is deposited. Thus, complete insulation is achieved only when all voids are filled. The aggregation coefficient between monomer molecules should generally be greater than that between monomer and substrate, so that growth of the film tends to occur perpendicularly to the surface rather than laterally. In con-
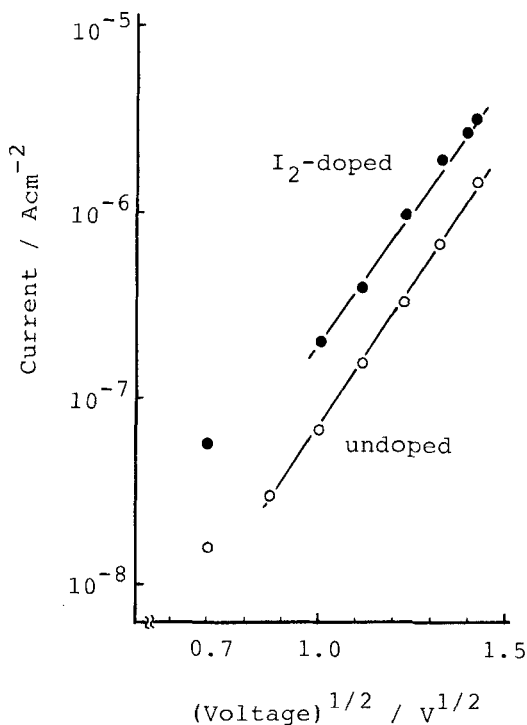
FIG. 6. Semilogarithmic plot of the forward-biased dark current vs (voltage)$^{1/2}$ of Al/plasma-polymerized CuPc film/ITO cells.

trast, in polymerization by plasma, the substrate is initially covered by the evaporated gas, which is almost simultaneously polymerized in situ. Further monomer molecules will be preferentially polymerized on any uncovered substrate surface due to their large kinetic and migration energies, and will consequently cover the substrate evenly. The lateral growth by plasma polymerization, as opposed to the perpendicular growth by vacuum deposition, allows continuous polymeric films with good rectification and insulation properties even when the film is as thin as 100 nm. Support for this mechanism, obtained from electrochemical properties, will be mentioned below.

    The pp-CuPc film obtained showed photovoltaic responses when light from a tungsten lamp shone through an IR cut-off filter onto a cell through Al electrodes. Photo J-V curves and characteristics parameters of photovoltaic cell (V_{oc},

TABLE 1. Photovoltaic Characteristics of Al/Plasma-Polymerized CuPc Films/ITO Cells[a]

Run	Plasma power, W	J_{sc}, nA/cm^2	V_{oc}, V	FF	η, %
A-1	30	10.4	0.36	0.20	1.23×10^{-5}
A-2	10	22	0.63	0.194	4.4×10^{-5}
A-3	2	42.7	0.60	0.19	8.01×10^{-5}
B-1	100	110	0.82	0.218	3.24×10^{-4}
B-2	30	400	0.90	0.138	8.18×10^{-4}

[a]The symbols are defined in the Experimental section.

J_{sc}, FF, and η) were obtained by changing the load resistance. The value of η in this report is for input light energy transmitted through Al. Upon illumination, Al always became negative against ITO. In general, the behavior or conversion efficiency was comparable to that of devices based on vacuum-deposited CuPc [10]. Since input light energy in this experiment reached a value as high as that of solar energy in daytime, higher values of η might be expected under lower illumination intensities [12, 13]. The short-circuit photocurrent from the cell always exhibits a fast (< 1 s) transient spike at the moment of illumination, followed by a gradual decrease over a period of minutes to a steady level.

Table 1 summarizes the effect of polymerization conditions on the photovoltaic characteristics of the cells. In both Methods A and B the performance parameters of the cell, V_{oc}, J_{sc}, and η, became less with increasing rf power in the polymerization. However, the parameters obtained by Method B always showed higher values than those by Method A. These results should be associated with the partial alteration of CuPc at high plasma power. In general, plasma energy can be associated with the relationship of W/FM [20], where W is the rf power, F is the flow rate, and M is the molecular weight of the gas supplied to the reaction chamber. It is reasonable to suppose that partial destruction of the CuPc structure occurs with high W/FM value, i.e., higher rf power or lower monomer supply. In the monomer-supply system used in our experiment, Method B can evaporate a larger amount of CuPc than Method A, which decreases the mean free path of energetic electrons in the glow discharge to give moderate plasma conditions accompanied by no extensive alteration of the ring structure.

Table 2 summarizes the photovoltaic properties of plasma-polymerized metal-free and metal-phthalocyanine films in sandwich cells.

TABLE 2. Photovoltaic Characteristics of Al/Plasma-Polymerized Metal Phthalocyanine Films/ITO Cells

Monomer	V_{oc}, V	J_{sc}, nA/cm^2	FF	η, %
H$_2$Pc	0.992	98.9	0.211	5.49×10^{-4}
CuPc	1.15	373	0.210	1.11×10^{-3}
NiPc	0.778	204	0.191	3.02×10^{-4}
MgPc	0.788	11.6	0.288	8.75×10^{-6}
ZnPc	0.986	9.12	0.267	1.38×10^{-5}

Electrochemical Properties

It has been reported that phthalocyanine thin films prepared by vacuum deposition show reversible oxidation and reduction in aqueous electrolyte solution and exhibits electrochromic characteristics [8]. We found that pp-CuPc films with certain pore channels, through which electrolytes can permeate, undergo oxidation to give rise to electrochromism although the behavior was irreversible. The pp-CuPc film of this type was specially prepared by simultaneous doping of iodine molecules. Iodine is known as a radical scavenger and, therefore, is assumed to be inactive toward plasma reaction. The I$_2$ molecules are mostly incorporated in dispersed molecular or cluster form in the polymer film. Immersion of the film in a large amount of ethanol to remove the doped iodine completely yielded a pp-CuPc film with micropores.

The lower end of the film was immersed into an electrolyte and the upper end was connected to an external circuit. A constant anodic current was applied and a color change from green to violet-brown was observed. The loss of electrons during this oxidation should be compensated by migration of anions (ClO$_4^-$ in this experiment) into the film. In order to maintain the charge balance of the film on oxidation, one or two electrons per oxidized species should enter into the film in the anion. Therefore, the rate and extent of oxidation are limited by the amount and velocity of the permeation of anions through the film, and these should be closely related to the pore size of the film. It should be emphasized, however, that no electrochromism and anodic current was observed for pp-CuPc film unless the film was prepared by simultaneous doping and subsequent removal of iodine molecules. In contrast, vacuum-deposited CuPc film, which is assumed to be porous in nature compared to the pp-CuPc film, showed electrochromism without iodine doping and a reversible color change from blue to violet. These ob-

servations indicate clearly that the pp-CuPc film, as distinct from porous build-up growth during vacuum deposition, provides uniform and pinhole-free coating on the glass electrode, and residual voids, if any, should be smaller than the hydrated electrolytes.

Catalytic Activity of Photoreduction

It was found that the pp-CuPc thus obtained exhibits high catalytic activity for photoreduction of solvated methyl viologen (MV^{2+}) on irradiation by visible light. Kaneko and coworkers discovered that metal phthalocyanine dispersed in a liquid phase caused reduction on irradiation with visible light in the presence of a reducing agent like EDTA; effects of solvent and of metal ions were investigated [28]. We carried out a comparable study of photore-duction with plasma-polymerized CuPc films and dispersed CuPc particles.

Figure 7 shows $MV^{\cdot+}$ formation catalyzed by pp-CuPc and "monomeric" CuPc particles in DMSO-H_2O mixture. No reduction occurred on irradiation with visible light unless catalyst was present in the medium. The pp-CuPc film shows almost the same activity as CuPc particles. Since the particle sur-
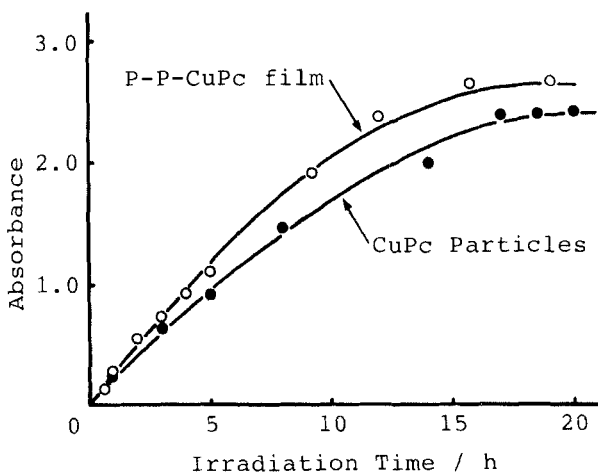

FIG. 7. Photoreduction of methyl viologen using plasma-polymerized CuPc film (○) or CuPc particles (●). Plasma-polymerized CuPc film, 0.8 mg; CuPc particles, 0.8 mg; methyl viologen, 0.5 mM; EDTA, 1.0 mM; solvent, DMSO containing 5 vol% water; 15°C; light intensity, 100 mW/cm².
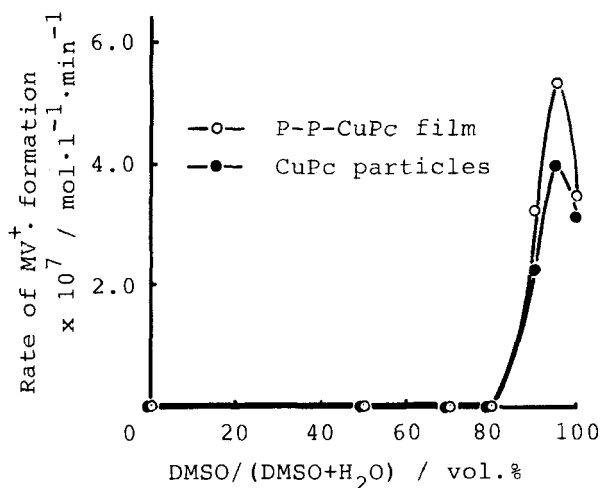
FIG. 8. Effect of DMSO concentration on the rate of photoreduction of methyl viologen. Plasma-polymerized CuPc film, 0.3 mg; CuPc particles, 0.3 mg; Methyl viologen, 0.5 mM; EDTA, 1.0 mM; 17°C; light intensity, 150 mW/cm^2.

face at which the reaction takes place should be less for pp-CuPc film than that for monomeric CuPc particles, the catalytic activity should be rather high.

Figure 8 shows the effect of DMSO concentration on the rate of $MV^{\cdot+}$ formation. It is seen that the rate for both cases shows a maximum at 95:5 DMSO/water, and the curves resemble each other. This indicates that the plasma-polymerized CuPc film retains the original catalytic activity of the monomer and that no extensive destruction or alteration of CuPc ring has taken place. The pp-CuPc film was used more than 20 times in the different conditions, and the activity did not decrease (Fig. 9). In addition, the polymeric film has the advantage that it does not contaminate the reaction medium and is easy to handle.
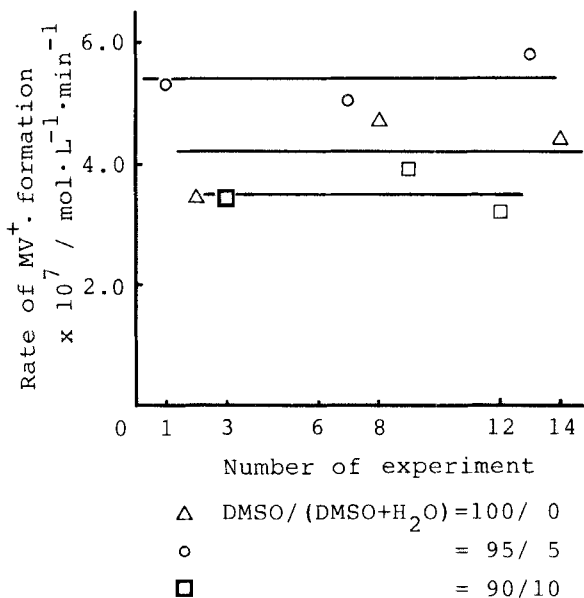
FIG. 9. Change in photocatalytic activity of plasma-polymerized CuPc films by repeated use. Plasma-polymerized CuPc film, 0.3 mg; methyl violo-gen, 0.5 mM; EDTA, 1.0 mM; 17°C; light intensity, 150 mW/cm^2.

ACKNOWLEDGMENTS

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