

# Dry-Process Recording Material by Use of Photosensitized Solid-State Reaction of *m*-Phenylenediacyrylic Acid

## INTRODUCTION

In various applications of holography practical recording materials with much excellent properties are required. For practical use in holographic interferometry the desired properties include high sensitivity, high resolution, high diffraction efficiency, dry developing, and fixation process and long shelf-life. Silver halide photographic emulsion and dichromated gelatine have not been found suitable for real-time holographic interferometry owing to the necessity of the wet developing process and the lack of moisture stability. Some photosensitive polymers with a dry developing process were reported.<sup>1-3</sup> However, their sensitivity was affected by intensity of the exposing light or oxygen. If recording materials with dry developing process become generally available, we can expect remarkable progress in application of holographic interferometry. Mizuno and Hattori<sup>4</sup> succeeded in such dry process holographic recording, using a crystalline material which utilized *m*-phenylenediacyrylic acid as a photosensitive crystal and picramide as a photosensitizer. The purpose of this study is to elucidate changes in chemical and physical properties of this new record material during exposure, thermal development, and fixation. An attempt to improve surface smoothness and durability of recording plate was also carried out.

## EXPERIMENTAL

Materials *m*-phenylenediacyrylic acid (*m*-PDA) was prepared according to Suzuki et al.<sup>5</sup> It was recrystallized from acetic acid, mp = 295°C,  $\lambda_{\max}$  = 272 nm ( $\epsilon$ : 54,500). All reagents used are of commercially available extra pure grade.

TABLE I  
Summary of Experimental Results on Photosensitive Material Comprising *m*-PDA and Picramide

Sample	DSC, endotherm at °C	UV, $\lambda$ max (nm)	IR	X-ray	Photore- action <sup>a</sup>
S-1 <i>m</i> -PDA	291	P <sub>1</sub> (257)	P <sub>1</sub>	P <sub>1</sub>	no
S-2 picramide	193	P <sub>2</sub> (413)	P <sub>2</sub>	P <sub>2</sub>	no
S-3 reprecipitate from 1:1 THF solution	191,258	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	yes
S-4 mixture of 1:1 crystals	191,260	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	yes
S-5 heat-treated S-3 <sup>b</sup>	191,259	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	yes
S-6 photoirradiated S-3	186	P <sub>2</sub> + P <sub>3</sub>	P <sub>2</sub> + P <sub>3</sub>	P <sub>2</sub>	—
S-7 heat-treated S-6 <sup>b</sup>	186	P <sub>2</sub> + P <sub>3</sub>	P <sub>2</sub> + P <sub>3</sub>	P <sub>2</sub>	—
S-8 1:1 mixture of S-3 and S-6	187	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	yes
S-9 heat-treated S-8 <sup>b</sup>	187	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	P <sub>1</sub> + P <sub>2</sub>	yes
S-10 <i>m</i> -PDA oligomer	none	P <sub>3</sub> (272)	P <sub>3</sub>	amorph.	—
S-11 photoproduct of S-3	215	P <sub>3</sub> + (P <sub>1</sub> )	P <sub>3</sub> + (P <sub>1</sub> )	nearly. amorph.	—

<sup>a</sup> Sample embedded in KBr matrix was photoirradiated with the light of wavelength longer than 430 nm.

<sup>b</sup> Sample was heat-treated at 130°C for 30 min.

### Preparation of Recording Plate

The optimum photosensitive solution contained 100 mg of *m*-PDA and 100 mg of picramide dissolved in 5 mL of tetrahydrofuran (THF). To improve surface smoothness, poly(methyl methacrylate) (PMMA) 200 mg was added to this solution. The photosensitive film was made in the following way: a 0.2-mL drop of photosensitive solution was dripped onto the glass plate ( $3.8 \times 2.6 \text{ cm}^2$ ). The drop was spread on the plate by revolution of a spinner at 1500 rpm. It dried instantly, forming a film of mixed microcrystals of each ingredient.

### Procedure for Hologram Formation and Printing of Patterns

To test the performance of the photosensitive plate as a recording material for holographic interferometry, holographic gratings were recorded on the plate using the optical arrangement with a 442-nm He-Cd laser as the recording light.

Exposure conditions consist of 50 s with power of  $25 \text{ mJ/cm}^2$ .

For testing of printing a mask film was put on the plate tightly, and it was exposed to light having wavelength longer than 430 nm for a few minutes to 60 min, using a 500-W Xenon lamp with filter (Corning Co., No. 3-72).

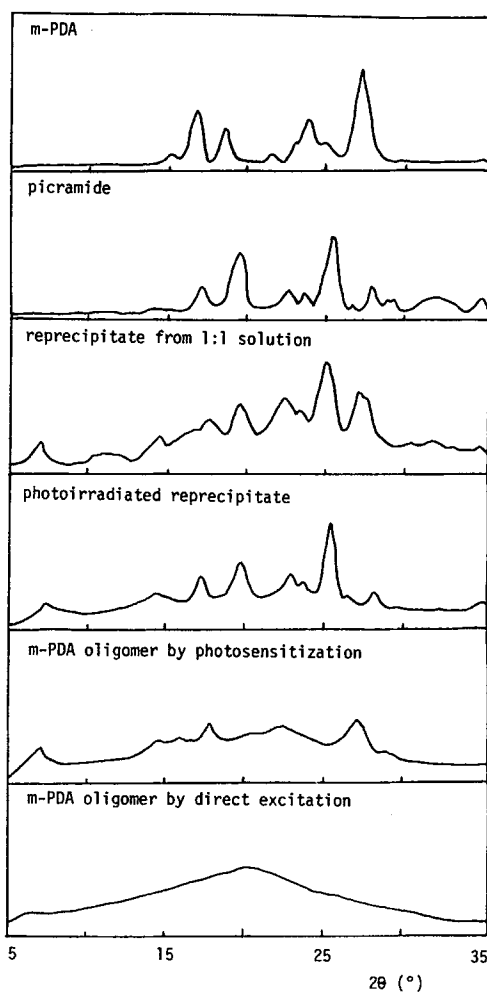


Fig. 1. X-ray powder diagrams of *m*-PDA, picramide and photosensitive materials before and after exposure.

### Heat Treatment

Photosensitive plates which were exposed to light or laser were kept in the oven at 120°C for 30 min.

### Photosensitized Reaction

The KBr pellet method was used to determine effective sensitizers and amounts for *m*-PDA. KBr pellets which contain *m*-PDA and sensitizer were irradiated with light of wavelength longer than 430 nm for several minutes to 2 h. The decrease of absorption of double bond ( $\nu_{C=C}$  1640  $\text{cm}^{-1}$ ) was followed by IR to measure the efficiency of different sensitizers.

For a typical reaction, the residue obtained by drying up the photosensitive solution was suspended in water (100 mL) and irradiated with light of wavelength longer than 430 nm. The reaction was followed by the IR and UV spectrum. Irradiated material was stirred in benzene to dissolve picramide in benzene. The white powder residue was examined by spectroscopic and molecular weight measurements.

## RESULTS AND DISCUSSION

### Photosensitive Material

It is known that picramide forms a molecular complex with some kinds of aromatic compounds.<sup>6</sup> The UV spectra of the THF solution of picramide and *m*-PDA were measured in various compositions to find out the possibility of complex formation. As the composition of solution was changed, absorption varied monotonously from one to the next, and none of the additional absorption peaks was observed. This means that there is no complex formation between picramide and *m*-PDA.

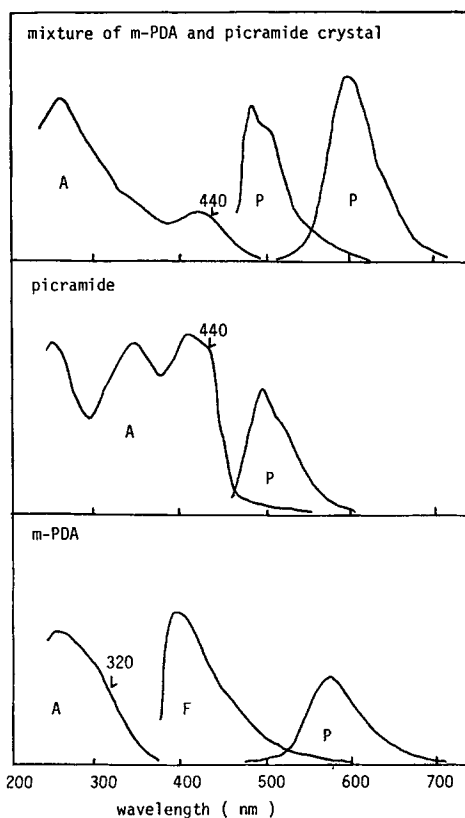
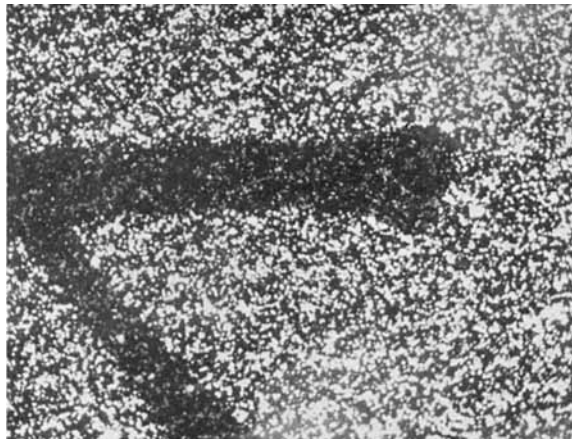


Fig. 2. Emission spectra of *m*-PDA, picramide and their 1:1 mixture. A:absorption; F:fluorescence; P:phosphorescence.



(1)



(2)

Fig. 3. Micrographs of photosensitive plates (1) after exposure and (2) after heating (78 $\times$ ).

X-ray powder diffraction patterns of *m*-PDA, picramide, and photosensitive material obtained by evaporating photosensitive solution and the mixture of *m*-PDA and picramide crystals are shown in Table I. IR, UV, and X-ray data on photosensitive material show that their peaks are additive patterns of each of these crystals, and they are consistent with those of the crystalline mixture. Two melting points of photosensitive material were measured by differential scanning calorimetry (DSC), which confirms that photosensitive material is a mixture of each compound.

From these data it is concluded that the photosensitive material is a simple aggregate of microcrystals of *m*-PDA and picramide.

#### Photosensitized Reaction

It was confirmed by the KBr pellet method that *m*-PDA and picramide crystals are stable when irradiated with light of wavelength longer than 430 nm. In the photosensitized reaction of *m*-PDA the decrease of C=C double bonds was rather slow compared with that of KBr pellet method.

X-ray powder diffraction patterns of photoirradiated material was nearly the same as those of picramide, indicating that *m*-PDA became amorphous by irradiation. In fact, the product obtained by removing picramide was nearly amorphous, though there were small amounts of unreacted *m*-PDA (Fig. 1).

The NMR spectrum of the product indicates the presence of cyclobutane rings. The number average molecular weight determined by vapor-pressure osmometry was about 1000.

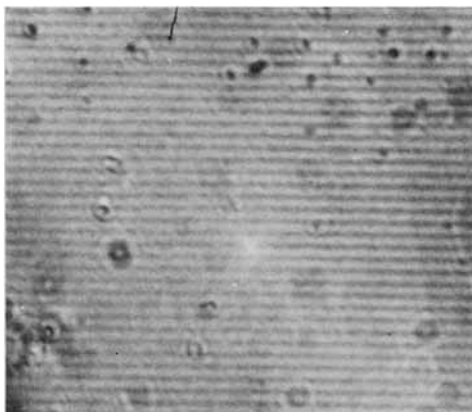


Fig. 4. Micrograph of recorded holographic gratings of 780 lines/mm (900 $\times$ ).

Judging from these data, it is concluded that the photoproduct is an amorphous oligomer obtained by cycloaddition reaction of double bonds similar to the four-center type photooligomerization of *m*-PDA crystal<sup>5</sup> proceeded by irradiation with shorter wavelengths.

#### Mechanism of Photosensitization

When *m*-PDA crystals were excited with light of wavelength 320 nm, fluorescence was observed at 400 nm and phosphorescence at 580 nm (Fig. 2). On the other hand, when picramide crystals were excited at 440 nm, only phosphorescence was observed at 500 nm. The mixture of *m*-PDA and picramide crystal, when irradiated with 440 nm, which *m*-PDA cannot absorb, gave phosphorescence of *m*-PDA at 580 nm as well as that of picramide at 500 nm. These data indicate that the oligomerization of *m*-PDA is stimulated by T-T energy transfer from picramide to *m*-PDA, predominantly through their contact surface and, to a lesser extent, inside the crystal.

#### Mixing ratio of *m*-PDA and Picramide

The effective amounts of picramide on the performance was measured using KBr pellets contained different ratios (weight) of *m*-PDA and picramide, i.e., 1:1, 1:0.1, and 1:0.01. When irradiated with light of wavelength longer than 430 nm, the IR absorption of double bonds in the latter two pellets scarcely changed after 1.5 h of irradiation; in the former, about 80% of double bonds disappeared. It seems that relatively large amounts of picramide are required to cover *m*-PDA crystals so as to achieve sufficient sensitization.

The effect of several other sensitizers on this reaction was examined. Among these 1,2-benzoanthraquinone and 2-nitrofluorene have some sensitizing effect, though they are less effective than picramide.

#### Heat Treatment

Spectroscopic data of photoirradiated material before and after heat treatment are shown in Table I. No remarkable differences were found in the spectroscopic data of the two samples. Clear differences, however, were seen in the clarity of printing (Fig. 3). Mask image is obscure to the eye just after exposure, but after heat treatment it becomes clearer. It was observed under a polarizing microscope that exposed parts were dark but became completely dark after the heat treatment, implying that the exposed parts became amorphous. This is also true for the case of a photosensitive plate composed of only *m*-PDA on which printing was made by exposure to wavelengths around 300 nm. It is likely that oligomers surrounded by the monomer cause a melting point depression so that exposed parts melt during the heat treatment, leading to glass formation. Development is performed by this phenomenon. When the weight of photosensitive plate was measured before and after heat treatment, it was found that 80–90% of picramide was sublimated off during the heating. This explains why fixation is accomplished by simple heat treatment.

**Photosensitive Plate Containing PMMA as a Binder**

The photosensitive plate has large crystal size and is sensitive to handling. To improve these disadvantages, a photosensitive plate containing a polymer as a binder was investigated. PMMA was selected because of its high solubility in a photosensitive solution. PMMA was added in various amounts (50, 200, and 600 mg) to solution of *m*-PDA (100 mg) and picramide (100 mg). Microscopic observation of plates made from these solutions showed that the size of microcrystals deposited was smaller. Crystal growth of picramide was especially suppressed by adding PMMA. In addition, these plates were quite resistant to hand-touching. The effect on resolution power was also checked. The plate containing 600 mg of PMMA failed to record holographic grating. In the case of 50 and 200 mg of PMMA gratings were fairly recorded with a resolving power of about 780 lines/mm (Fig. 4). The same resolving power as that without PMMA (2000 lines/mm) was not attained. However, considering the improvement in handling, photosensitive plates with 200 mg of PMMA are suitable for practical use.

**References**

1. J. M. Moran and I. P. Kaminow, *Appl. Opt.*, **12**, 1964 (1973).
2. L. Booth, *Appl. Opt.*, **14**, 378 (1972).
3. J. Tomlison, E. A. Chandross, H. P. Weber, and G. D. Aumiller, *Appl. Opt.*, **15**, 534 (1976).
4. T. Mizuno, S. Hattori, and M. Tawata, *J. Opt. Soc. Am.*, **67**, 1651 (1977).
5. F. Suzuki, Y. Suzuki, H. Nakanishi, and M. Hasegawa, *J. Polym. Sci. A-1*, **7**, 2319 (1969).
6. T. Asahina and T. Shinomiya, *Nippon Kagaku Kaishi*, **59**, 341 (1938).

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