

# Highly concentrated phenanthrenequinone-doped poly(MMA-co-ACMO) for volume holography

Fenglan Fan (范凤兰)<sup>1,2</sup>, Ying Liu (刘颖)<sup>1</sup>, Yifan Hong (洪一凡)<sup>1</sup>, Jinliang Zang (臧金亮)<sup>1</sup>, Guoguo Kang (康果果)<sup>1</sup>, Tianbo Zhao (赵天波)<sup>2,\*\*</sup>, and Xiaodi Tan (谭小地)<sup>3,\*</sup>

<sup>1</sup>*School of Optoelectronics, Beijing Institute of Technology, Beijing 100081, China*

<sup>2</sup>*Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China*

<sup>3</sup>*Fujian Provincial Key Laboratory of Photonics Technology, College of Photonic and Electronic Engineering, Fujian Normal University, Fuzhou 350007, China*

\*Corresponding author: [xtan@fjnu.edu.cn](mailto:xtan@fjnu.edu.cn); \*\*corresponding author: [bit\\_bipt@126.com](mailto:bit_bipt@126.com)

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Novel composite materials are synthesized by incorporating N-acryloylmorpholine (ACMO) in highly concentrated phenanthrenequinone (PQ) doped poly(methyl methacrylate) (PMMA). The photosensitizer concentration of PQ was increased from 0.7 wt. % to 1.8 wt. %. The doping of ACMO component results in a higher diffraction efficiency and photosensitivity than a typical PQ/PMMA system. The enhanced performance of the material may stem from the ACMO molecules, which might open a new route for improving the holographic performance of the PQ/PMMA photopolymer.

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A widespread consensus has been reached that volume holographic data storage is one of the most potential next generation storage techniques due to its large capacity and high data transfer rate<sup>[1,2]</sup>. For volume holographic storage using thick materials, good optical quality and dimensional stability are the most fundamental requirements<sup>[3,4]</sup>. Among the current recording materials, photopolymer materials are the most popular and suitable for the volume holographic write-once-read-only-memory system. Specifically, phenanthrenequinone (PQ) doped poly(methyl methacrylate) (PMMA) photopolymer deserves much attention owing to its remarkable advantages, such as controllable thickness, good optical quality, and negligible shrinkage (shrinkage coefficient  $< 10^{-5}$ ) when exposed to light<sup>[5-7]</sup>.

Currently, the common preparation method for thick PQ/PMMA photopolymer material is the thermal polymerization method, dissolving photosensitizer PQ into the MMA solution, which is the polymerizable monomer. However, due to the low saturation concentration of PQ dissolved in MMA<sup>[8]</sup>, compared with other materials, PQ/PMMA has the drawbacks of a lower diffraction efficiency and sensitivity. It is known that the general method to enhance the photosensitivity and obtain a high diffraction efficiency is to improve the photosensitizer concentration. But PQ's concentration in the PQ/PMMA material is limited by the restricted solubility of PQ in the MMA monomer. To the best of our knowledge, although some investigations have been conducted to improve properties of PQ/PMMA by doping other material like nanoparticles<sup>[9]</sup>, nitroaniline<sup>[10]</sup>, and an organic metallic component<sup>[11]</sup>, these methods have not achieved the improvement of solubility.

In this paper, for the first time, we introduced ACMO into PQ/PMMA material to increase the concentration of PQ. ACMO is an acrylate monomer that has shown a good compatibility with the MMA. In particular, the dissolving capacity is nearly five times higher than that of the MMA monomer for the PQ molecule. After introducing ACMO into the PQ/PMMA material, the photosensitizer concentration of PQ was increased from 0.7 wt. % to 1.8 wt. % compared to the typical PQ/PMMA sample. Then the volume holographic characteristics and the corresponding physical mechanism in the PQ-doped poly(MMA-co-ACMO) photopolymer were experimentally investigated.

Thick samples were prepared by the thermal polymerization method. All chemicals were purchased from Macklin and used without further purification. The chemical structures are displayed in Fig. 1. First, the monomers MMA and ACMO were mixed together in definite proportions with mass ratios of 1:9 (A1M9) and 2:8 (A2M8). Second, we dissolved the powder of PQ and thermal initiator 2,2-azobisisobutyronitrile (AIBN) into the monomer mixture (MMA and ACMO) solution. The resulting solution was stirred with a magneto stirrer in a glass bottle at 35°C for about 10 min until it became a homogenous solution. Then the solution was stirred at 60°C until it turned highly viscous. The viscous solution was poured into a glass mold, back at 45°C for 7 days, and became a self-sustained solid block. The resulting yellowish bulk photopolymer had a thickness of 1.5 mm for which the optical quality is suitable for the experiment of holographic recording.

In the thermal polymerization stage (during material preparation), monomers were polymerized using AIBN

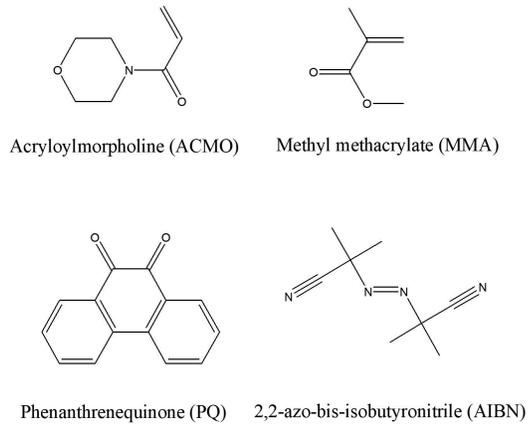
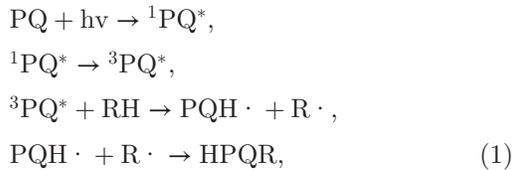


Fig. 1. Chemical structures of the components in our photopolymer.

as the initiating system. Most of the monomers molecules ( $\sim 90\%$ ) can be polymerized in this stage, leading to the formation of a polymer matrix. The unreacted monomers, together with PQ, were uniformly distributed in the polymer matrix<sup>[4]</sup>.

In the photoreaction stage (during optical exposure), PQ can absorb energy as a photosensitive molecule to form an excited state. Then, the excited PQ molecules receive a hydrogen atom from H donors (RH), which results in the formation of semiquinone radical  $\text{PQH}\cdot$  and donor derived radical  $\text{R}\cdot$ . Subsequently, the radical enables the reaction with the carbonic double bond on the monomer molecule, which forms the photoproducts:



where  ${}^1\text{PQ}$  and  ${}^3\text{PQ}$  phenanthrenequinone are in the singlet and triplet excited states, respectively; HPQ is the semiquinone radical; RH is the hydrogen donor represented by the monomer molecules.

For the traditional holographic recording, the primary chemical reaction occurs in the bright region of the interference fringes. Free PQ and monomer molecules diffuse from the dark region into the bright region. As a result, the refractive index in the bright region is different from that in the dark region, hence the phase grating can be formed in such a system through photoreaction<sup>[12]</sup>. Based on this process, our method is feasible for improving the holographic characteristics by increasing the concentration of PQ, which could be used to affect the photoreaction between PQ and the monomer.

UV-Vis spectra of the photopolymer were recorded using a U-1901 double-beam spectrometer. Figure 2 presents typical optical absorption spectra of the photopolymer incorporating the various doping components in both unexposed states. PQ served as the only major photosensitizer in the photopolymers<sup>[13]</sup>. Therefore, the

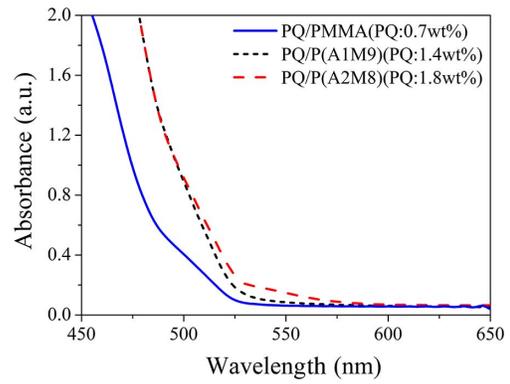


Fig. 2. Optical absorption spectra of different samples doped with different PQ concentration photopolymers.

concentration of PQ is an important factor related to the absorption responses of photopolymer.

As shown in Fig. 2, before exposure, the absorption coefficients of PQ/PMMA, PQ/P(A1M9), and PQ/P(A2M8) are  $\alpha = 0.076$ ,  $0.127$ , and  $0.196 \text{ cm}^{-1}$  at  $\lambda = 532 \text{ nm}$ , respectively. It is noted that a higher concentration of PQ leads to a higher absorption value. Furthermore, it indicates that the concentration of PQ was increased successfully by introducing ACMO into the PQ/PMMA photopolymer in contrast to the restricted solubility (0.7 wt. %) in the MMA monomer.

In order to study the hologram recording capability of our photopolymer samples, we built an optical system, as shown in Fig. 3. A green laser beam (532 nm) from a diode-pumped solid state Nd:YAG laser was collimated and split into two beams with the equal intensity of  $52 \text{ mW/cm}^2$ . One beam (signal beam) was controlled by a shutter (shutter 2) for switching between the recording process and the reconstruction process. These two beams were incident into the sample symmetrically with a cross angle of  $30^\circ$  in a common incident plane. The diffraction efficiency ( $\eta$ ) is calculated by

$$\eta = \frac{I_d}{I_0}, \quad (2)$$

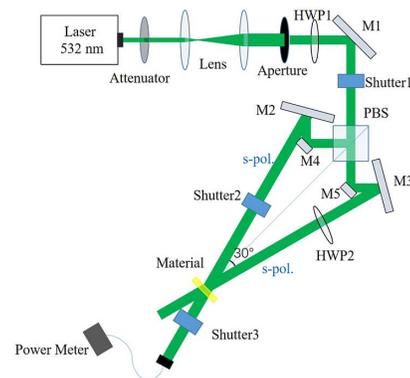


Fig. 3. Schematic of experimental setup. M: mirror; HWP: half-wave plate; PBS: polarizing beam splitter.

where  $I_d$  and  $I_0$  are the diffracted and incident intensities, respectively.

Figure 4(a) shows the temporal evolution of the diffraction efficiencies for our new material and PQ/PMMA. It should be noted that the diffraction efficiency of ACMO-doped PQ-PMMA is much higher than that of PQ/PMMA. For photopolymer PQ/A1M9 and PQ/A2M8, the diffraction efficiency increases with increasing concentration of PQ and ACMO. In addition, we also calculated the recording sensitivities ( $S$ ) of photopolymers during 150 s from the beginning of recording. For photopolymers PQ/A1M9 and PQ/A2M8,  $S$  are 0.33 and 0.42 cm<sup>2</sup>/J, which have been improved 3 and 4 times higher than that of PQ/PMMA, respectively. The speed of holographic formation became higher with the increase of ACMO concentration.

Figure 4(b) shows the comparison of the diffraction efficiency among the three kinds of samples, with the same PQ concentration at 0.7 wt. % but different mass ratios of MMA and ACMO. The diffraction efficiency increases with increasing of ACMO content. It indicates that the enhancement of the diffraction efficiency was realized as the result of the additional refractive modulation in the bright region and dark region with the introduction of ACMO.

In the following, we discuss the underlying mechanisms of ACMO effects in holographic recording by infrared (IR) spectroscopy. IR absorption spectra were recorded from

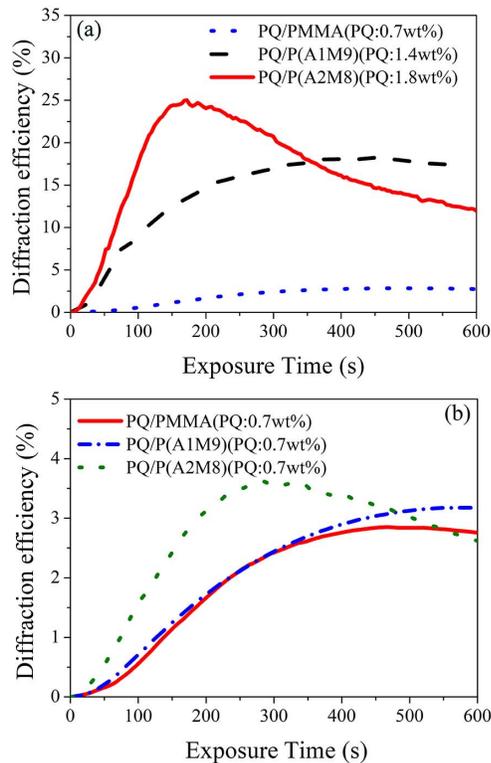


Fig. 4. Dependence of the orthogonal linear grating diffraction efficiency on the exposure time.

4000 to 500 cm<sup>-1</sup> using a Thermo IS5 spectrophotometer. Before measurement, the exposed PQ/MMA and PQ/A2M8 solutions were dipped on KBr plates. Here, the “exposed” samples were those that had been illuminated with laser beam with a wavelength of 532 nm. The plate sample was baked at 50°C for 5 h such that the unreacted monomer molecules were released and the photoproducts were left on the KBr plates.

For PQ/MMA, a band at 1736 cm<sup>-1</sup> can be observed from Fig. 5(a) after light exposure, which is ascribed to the absorption of C=O in the acrylate part of the photoproduct<sup>[14]</sup>. The absorption band at around 1630 cm<sup>-1</sup> could be attributed to C=O in the carbonyl group or C=C in the aromatic ring of the photoproduct. The bands at ~1245 and 1078 cm<sup>-1</sup> are ascribed to the C-O-C groups of the photoproducts on the PQ molecule reacting with the vinyl group on the MMA molecule. The possible structure of the photoproduct is shown in Fig. 6[(1)].

For ACMO, the absorption bands at around ~2950 cm<sup>-1</sup> (C-H stretches associated with the CH<sub>2</sub> species in the morpholine moiety), 1637 cm<sup>-1</sup> N-C=O stretching vibrations<sup>[15]</sup>, 1236 cm<sup>-1</sup> (C-O stretch within morpholine moiety), 1456 cm<sup>-1</sup> (C-N stretching vibration), and 1115 cm<sup>-1</sup> (C-O-C stretch within morpholine moiety) could be attributed to the characteristic structural vibrations of ACMO<sup>[15,16]</sup>.

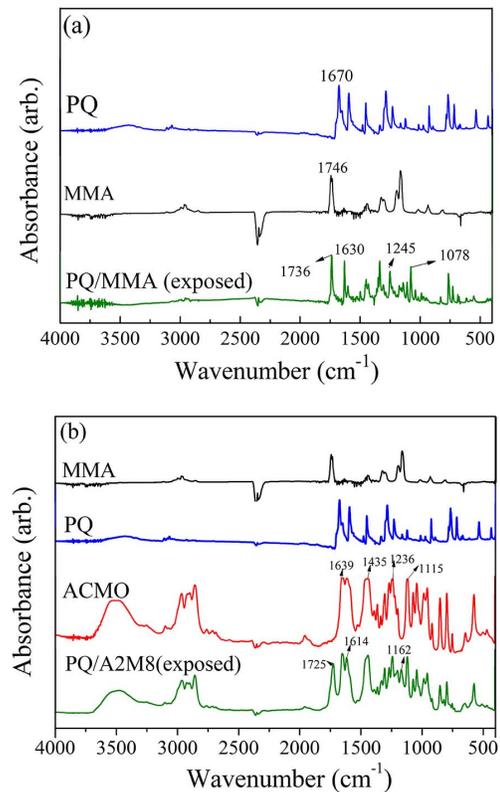


Fig. 5. Fourier transform infrared absorption spectra of PQ, monomers, and photoproducts.

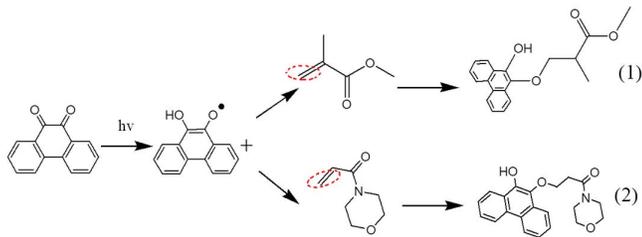


Fig. 6. Two kinds of different photoproducts (PQ attachment to the different monomer).

For the PQ/A2M8, the bands at 2950, 1435, 1236, and  $1115\text{ cm}^{-1}$  belong to the characteristic structural peaks of ACMO<sup>[17]</sup> and show that the structure of ACMO remains unchanged after exposure. However, compared with Fig. 5(a), the same peaks of photoproduct as PQ/MMA were not observed. This result proves that the ACMO has an influence on photoreaction of MMA and PQ under exposure. Some new peaks appear at wavenumbers  $\sim 1725$ , 1614, and  $1162\text{ cm}^{-1}$  that maybe belong to the new photoproduct [see Fig. 6,(2)] from the reaction between ACMO and PQ.

These phenomena show that ACMO is more active than MMA, and preferentially participates in a chemical reaction with PQ to form photoproduct (2) in the bright region. Monomers and PQ would be redistributed in the material through the diffusion process during exposure (Fig. 7), which can lead to a concentration gradient and chemical component change in the bright region and the dark region to produce a refractive index change for the traditional holographic recording. Therefore, the diffraction efficiency was increased with the increasing of ACMO content.

We investigated the real image reconstruction characteristics of the PQ/P(A2M8) photopolymers. In the experiment, the signal wave and reference wave were both s-polarized. The dimension of the PQ/P(A2M8) sample was approximately  $10\text{ mm} \times 10\text{ mm} \times 15\text{ mm}$ .

Figure 8(a) shows a photograph of a directly transmitted image through the optical system. Figure 8(b) shows the image that was reconstructed by the hologram recorded in PQ/P(A2M8). The images have the same  $305\text{ pixel} \times 305\text{ pixel}$ . As we can see, the reconstructed

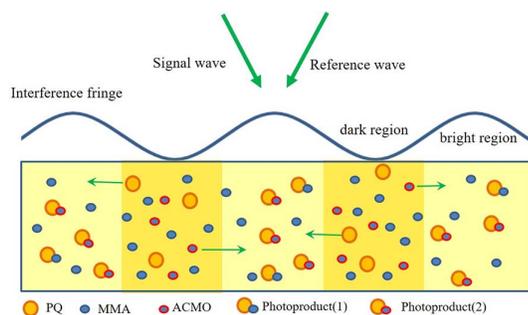


Fig. 7. Holographic diffusion process during exposure.

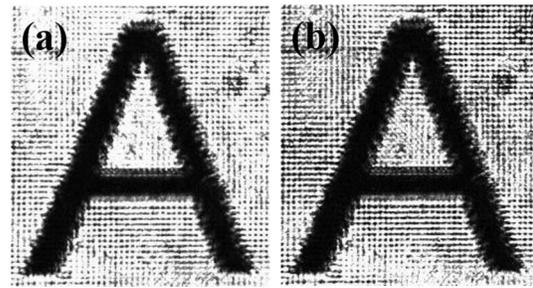


Fig. 8. Image reconstruction results in traditional holography system: (a) original transmitted image and (b) reconstructed image.

image maintains a very good contrast and high fidelity, which demonstrates that our material possesses the ability of information recording. This result shows our new photopolymer owns the potential of practical application in volume holographic storage.

In this work, we provided an effective pathway to improve the performance of PQ/PMMA by overcoming the solubility limit of PQ. Introducing ACMO is an effective method for improving the concentration of PQ (up to 1.8 wt. %). The evident improvement of the holographic sensing response and diffraction efficiency is demonstrated experimentally. These results suggest that our composite materials provide a significant foundation for enhancing the applicability of PQ/PMMA photopolymer in permanent volume holographic storage.

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