

Holographic Recording Characteristics and Physical Mechanism of Zinc Methacrylate/Nitroaniline-co-doped Poly(methyl methacrylate)/9,10-Phenanthrenequinone Photopolymers

Cheng-Jung Ko,¹ Po-Lin Chen,² Yi-Nan Hsiao,² Shiu-an-Huei Lin,³ Wha-Tzong Whang,¹ Ken Y. Hsu,² Kuo-Jung Huang,¹ Chun-Chao Chen,¹ I-Hsiang Tseng,⁴ Mei-Hui Tsai⁴

¹ Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsin-Chu 300, Taiwan, Republic of China

² Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsin-Chu 300, Taiwan, Republic of China

³ Department of Electrophysics, National Chiao Tung University, Hsin-Chu 300, Taiwan, Republic of China

⁴ Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan, Republic of China

In this study we developed an approach to improve the characteristics of photopolymers for holographic data storage. Through codoping different compounds, *N,N*-dimethyl-4-nitroaniline (DMNA) and zinc methacrylate ($\text{Zn}(\text{MA})_2$), into 9,10-phenanthrenequinone (PQ) doped poly(methyl methacrylate) (PMMA), the diffraction efficiency and the value of dynamic range ($M\#$) have been progressed. We enhanced the diffraction efficiency (from 36.1 to 86.2%) and the dynamic range ($M\#$, from 2.9 to 10.7) of PQ-doped PMMA through codoping with DMNA and $\text{Zn}(\text{MA})_2$. Using mass spectrometry and X-ray photoelectron spectroscopy, we investigated the mechanism behind the improvements in optical storage induced by the presence of $\text{Zn}(\text{MA})_2$ and DMNA in PMMA/PQ. POLYM. ENG. SCI., 53:1297–1305, 2013. © 2012 Society of Plastics Engineers

INTRODUCTION

Volume holographic recording is a promising data storage technology because it allows rapid data access with excellent storage capacity. The nature of the recording

medium plays a key role in the realization of this promising technology; photopolymers appear to be the most suitable materials [1–9]. Among the photopolymers tested, poly(methyl methacrylate) (PMMA)-based polymers have attracted the most attention because of their superior optical qualities, high flexibility, and negligible shrinkage when exposed to light [8–13].

Doping 9,10-phenanthrenequinone (PQ) into PMMA provides a holographic recording material from which holographic gratings have been fabricated [8–15]. The recording mechanism of the grating involves reactions between the PQ molecules and residual MMA monomer. Doping with organometallic compounds, such as zinc methacrylate [$\text{Zn}(\text{MA})_2$] [16–20], can be used to improve the holographic recording characteristics of PMMA/PQ photopolymers. The addition of $\text{Zn}(\text{MA})_2$ is not only to provide a catalyst to enhance the photoreaction between PQ and MMA molecules via the Zn ions in the $\text{Zn}(\text{MA})_2$ molecules, but also increase the number of reactants for photoreaction [16, 20]. Both reactions are effective for improving the sensitivity and dynamic range for holographic recording characteristics. Alternatively, doping with PQ-based derivatives can also improve holographic data storage [9]. For example, the presence of electron donor groups that accelerate the photoreaction can increase the recording sensitivity; on the other hand, the electron-accepting nitro group (NO_2) of 2-nitrophenanthrenequinone results in diffusely distributed electrons

Correspondence to: Y.-N. Hsiao; e-mail: davidshiao@gmail.com or W.-T. Whang; e-mail: wtwhang@mail.nctu.edu.tw

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and increases the birefringence effect of the sample, thereby improving its holographic characteristics.

Nitroaniline compounds, which are simple nonlinear optical (NLO) materials [21–23], possess both electron donor and acceptor groups within their structures. In a previous study [23], there were three different nitroaniline compounds ((4-nitroaniline; pNA), (*N*-Methyl-4-nitroaniline; MNA) and [*N,N*-Dimethyl-4-nitroaniline; DMNA]) codoped into the PMMA/PQ photopolymer. Investigations show that the PMMA/PQ/DMNA photopolymer had greatest holographic characteristics than pNA and MNA system. After light exposed, the pNA and MNA compounds predictably react with PQ to form new photoproducts. These new photoproducts would be providing a larger birefringence change and superior holographic recording performance. On the other hand, the DMNA did not react with either MMA or PQ to form new photoproducts when exposed to light. In the PMMA/PQ/DMNA system, the coexisting DMNA molecules affected the polarizability of PQ during the recording process [23, 24], which induces larger birefringence effects, thereby, improves the holographic characteristics. We suspected that doping with nitroaniline compounds possessing larger birefringence effects would improve the holographic characteristics.

In addition, the metal ion (Li^+ , Na^+ , Cu^{2+} , Zn^{2+}) was interacted with the nitroaniline to form other compounds and the dipole moment of compounds can be increased [25–27]. The compounds with a higher dipole moment led to higher birefringence by the exposed samples and increased the holographic recording characteristics. Therefore, taking advantage of previous research [9, 16–23], in this study we codoped $\text{Zn}(\text{MA})_2$ and nitroaniline into the PMMA/PQ photopolymer to enhance its holographic storage capacity and recording characteristics, as measured in terms of diffraction efficiency and dynamic range ($M\#$). We also propose herein a recording mechanism, deduced from mass spectrometric and X-ray photoelectron spectroscopic analyses. Our results indicate that the presence of both $\text{Zn}(\text{MA})_2$ and nitroaniline within PMMA/PQ photopolymers can significantly improve the dynamic range and sensitivity.

EXPERIMENTAL

Materials

$\text{Zn}(\text{MA})_2$ (Sigma–Aldrich) was dried in a vacuum oven at 110°C for 12 h. 2,2'-Azobisisobutyronitrile (AIBN; Showa) was purified through recrystallization from ethanol (99.5%). Methyl methacrylate (MMA; Showa) was distilled at low pressure to remove the stabilizer and then kept in a refrigerator until required for use. PQ (Tokyo Chemical Industry) was used as received. DMNA (98%) was obtained from Tokyo Chemical Industry. *N*-Methyl-4-nitroaniline (MNA, 97%) and 4-nitroaniline (pNA,

98%) were purchased from Alfa Aesar. The chemical structures of these compounds are provided in Fig. 1.

Photopolymer Fabrication

$\text{Zn}(\text{MA})_2$ (0.35 wt%) was dissolved in the MMA monomer completely through ultrasonication in a bath for 2 h. AIBN (2 wt%) was added to this solution, which was then stirred at room temperature for 2 h. Next, PQ (0.7 wt%) and a nitroaniline compound (PQ-to-nitroaniline molar ratio: 1:1) were added into the solution, which was then stirred for 6 h. The mixed solution was filtered (pore size: $0.2\ \mu\text{m}$) and stirred at 35°C for 12 h until the solution turned highly viscous. Finally, the viscous solution was poured into a glass cell and baked at 40°C for 3 days. A yellowish bulk photopolymer having a thickness of 2 mm and good optical quality with negligible photochemical shrinkage was obtained [13].

Measurements

To identify the mechanism of action and the recording characteristics of the various codoped PMMA/PQ photopolymer samples, all measurements were performed individually both before and after light exposure. UV–Vis spectra of the photopolymer were recorded using a Shimadzu UV-1800 spectrometer. The transverse electric (TE) and transverse magnetic (TM) refractive indices of the prepared photopolymers were measured using a prism coupler (Metricon Model 2010) at a wavelength of 632.8 nm. The birefringence (Δn), defined as the difference between the values of n_{TE} and n_{TM} , was also calculated. Mass spectra were recorded using a MICROMASS TRIO-2000 mass spectrometer. X-ray photoelectron spectra of the nitrogen and oxygen elements in the exposed photopolymers were recorded using a Microlab 350 instrument, operated in the constant analyzer energy mode with a pass energy of 40 eV and Mg $K\alpha$ (1253.6 eV) radiation as the excitation source. X-ray photoelectron spectroscopic analysis was performed at room temperature and under vacuum at pressures of less than 10–8 torr.

For measurements of holographic characteristic, a collimated light beam from an Ar laser (wavelength: 514 nm) was divided into two s-polarization beams (intensity of each beam: $5\ \text{mW}/\text{cm}^2$; ratio: 1:1; beam diameter: 0.7 cm). The intensity of the diffraction beam was detected when the shutter had blocked one of the beams. The two incident beams entered the samples symmetrically with an intersection angle, outside of the sample, of 30° . The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam to that of the summation of the diffracted beam and the transmitted beam. For measurements of the dynamic range, the photopolymers were placed on a rotational stage and multiple holograms were recorded using the perstrophic multiplexing technique. The exposed energy of each hologram was $0.52\ \text{J}/\text{cm}^2$.

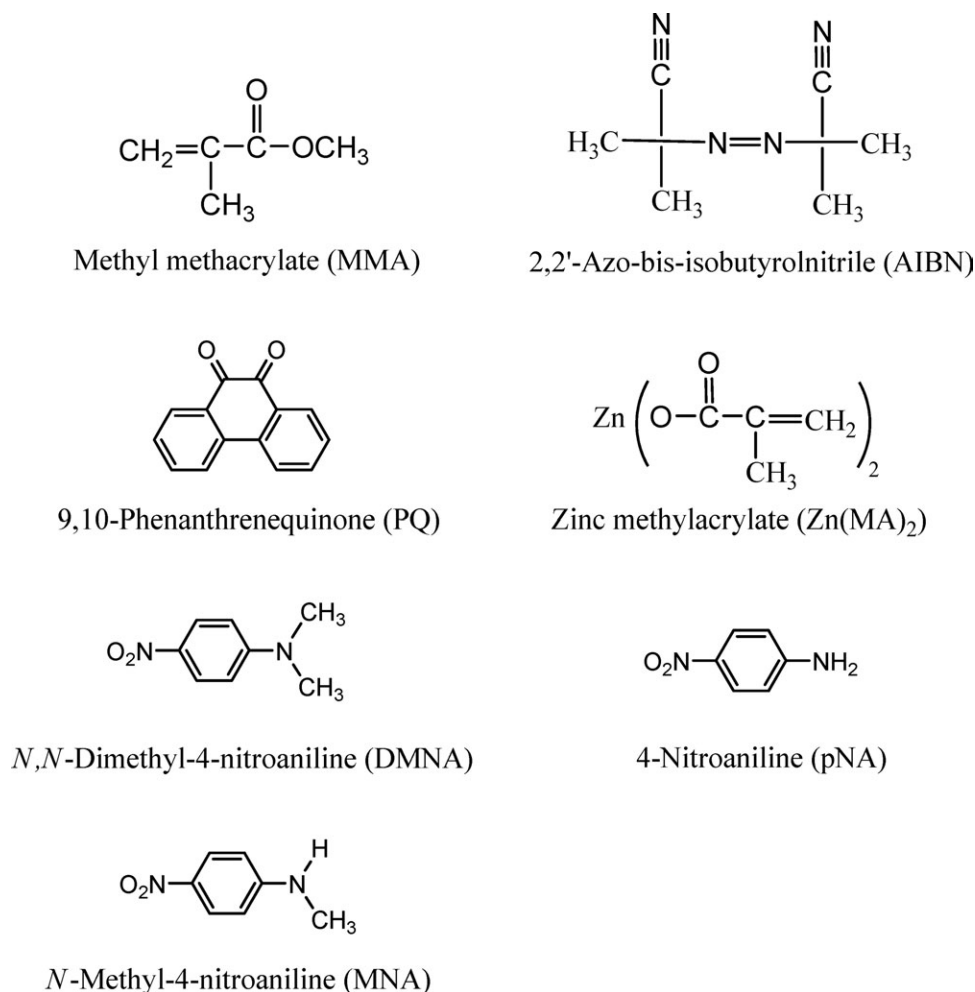


FIG. 1. Chemical structures of the compounds used in this study.

RESULTS AND DISCUSSION

Optical Properties of PMMA/PQ/Nitroaniline Photopolymers

Figure 2a displays typical optical absorption spectra of PMMA/PQ/nitroaniline photopolymers in their unexposed and exposed states (unexposed samples were analyzed immediately after fabrication; exposed samples had been illuminated at 514 nm for a suitable length of time). The signals of all of the photopolymers (PMMA/PQ, PMMA/PQ/pNA, PMMA/PQ/MNA, PMMA/PQ/DMNA) underwent a blue shift to shorter wavelength after exposure. The strong blue shifts imply that the photoproducts were less conjugated than those of the unexposed photopolymers, consistent with our previous studies [8, 23]. To observe the effects of doping nitroaniline compounds into PMMA/PQ, we tested the sensitivity and dynamic range of holographic recordings performed at 514 nm.

Diffraction Efficiencies of PMMA/PQ/Nitroaniline Photopolymers

Figure 3 displays the holographic diffraction efficiencies of the PMMA/PQ/nitroaniline photopolymers. The

samples of PMMA/PQ codoped with DMNA, pNA, and MNA exhibited maximum diffraction efficiencies of 60.3, 50.2, and 44.3%, respectively, significant improvements over that of the PQ-only doped photopolymer (36.1%). We suspect that doping with the nitroaniline compounds increased the birefringence of the photopolymer, such that its diffraction efficiency increased [9, 23]. Our previous study [23] has demonstrated that in the PMMA/PQ/nitroaniline systems, DMNA increased the birefringence of the photopolymer to a greater extent than did either pNA or MNA. Through this demonstration of the holographic data storage characteristics, we confirm that the properties of the PMMA/PQ photopolymer were further enhanced in the presence of DMNA [23]. On the basis of this result, and taking advantage of previous findings [16–23], we selected DMNA for codoping with the organometallic compound Zn(MA)₂ into the PMMA/PQ photopolymer.

Optical Properties of Codoped Zn(MA)₂ Photopolymers

Figure 2b presents typical optical absorption spectra of photopolymers codoped with Zn(MA)₂. After light exposure, the signals of all of the exposed photopolymers

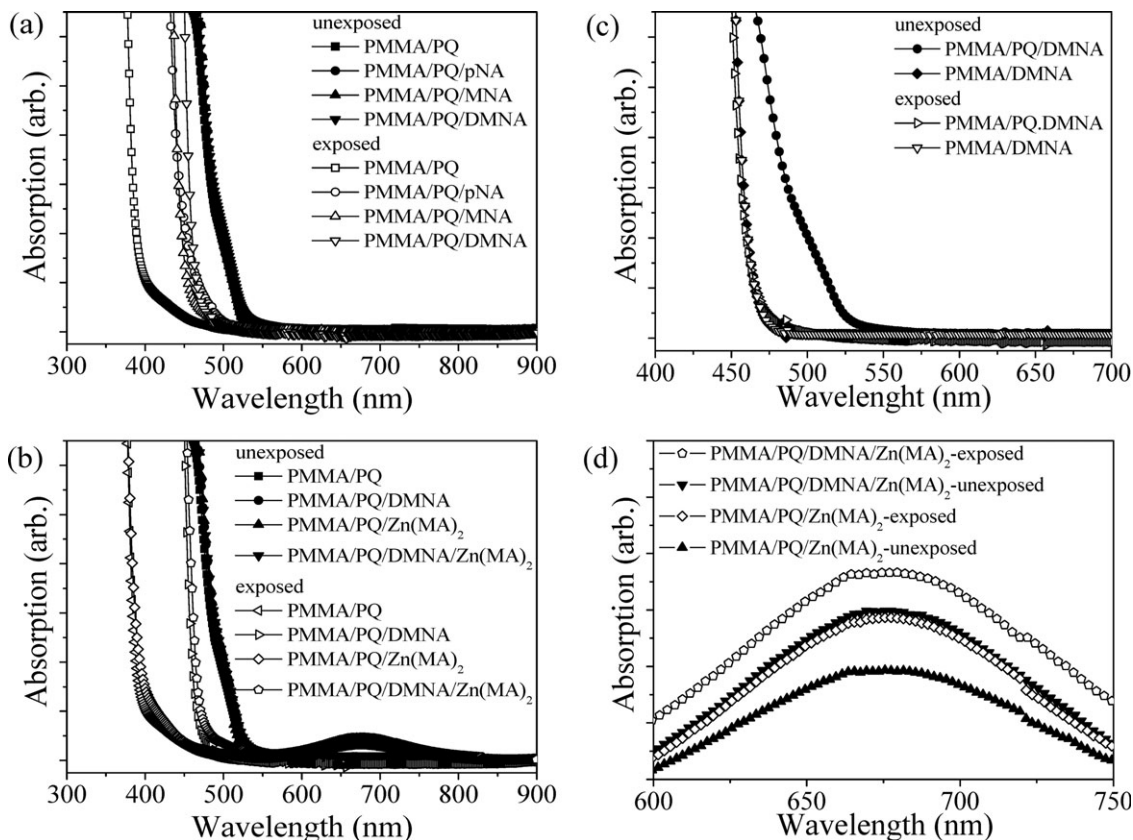


FIG. 2. UV-Vis absorption spectra of the (a) unexposed and exposed PMMA/PQ/nitroaniline photopolymers; (b) unexposed and exposed photopolymers and (c) DMNA-only doped photopolymers (without PQ); (d) expanded region of a portion of the long wavelength range.

underwent blue shifts to shorter wavelengths, again implying that the photoproducts were less conjugated than the species present in the unexposed photopolymers [8, 9, 13, 20]. The absorption bands of the exposed codoped DMNA samples were close to that of the DMNA-only doped photopolymer (Fig. 2c). In their unexposed states, all of the photopolymers in Fig. 2b provided similar absorption at 514 nm, suggesting that PQ served as the only major photosensitizer in the various codoped photopolymers.

The photopolymers doped with Zn(MA)₂ also exhibited small absorbances from 600 to 750 nm; Fig. 2d displays the corresponding expanded regions of the spectra. The absorption intensity in this range increased after light exposure, implying that Zn(MA)₂ reacted with PQ to form other photoproducts [17, 20]. Comparing the absorption intensities of the unexposed PMMA/PQ/DMNA/Zn(MA)₂ photopolymer and the unexposed PMMA/PQ/Zn(MA)₂ photopolymer, we find that the sample codoped with DMNA provided a stronger absorption, suggesting that some of the Zn(MA)₂ species may have interacted with DMNA molecules to form other compounds prior to light exposure [28]. Subsequently, after light exposure, the intensity of each curve increased, presumably because the remaining Zn(MA)₂ species reacted with PQ to form other photoproducts [17, 20]. A variation in molecular structure is the main effect leading to a refractive index

or birefringence change for grating recording in photopolymers. To observe the effect of Zn(MA)₂ and DMNA doping in the PMMA/PQ, in this study we characterized the sensitivity and dynamic range using 514 nm as the recording wavelength.

Table 1 lists the values of the birefringence ($\Delta n = n_{TE} - n_{TM}$) of the photopolymers codoped with Zn(MA)₂. The

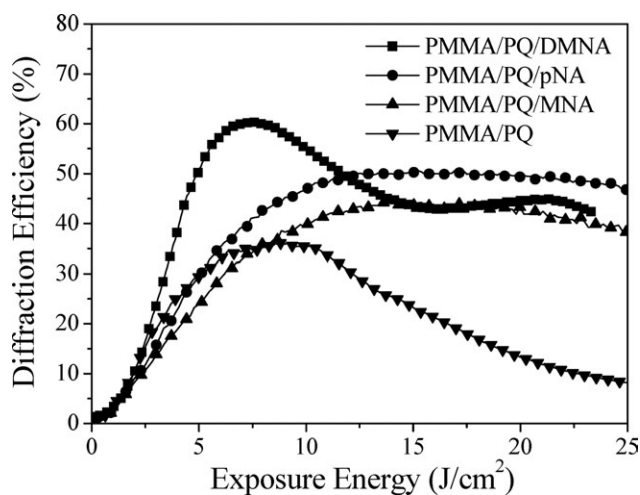


FIG. 3. Holographic diffraction efficiencies of the PMMA/PQ/nitroaniline photopolymers.

TABLE 1. Birefringence of the exposed photopolymers.

Sample	n_{TE} (632.8 nm)	n_{TM} (632.8 nm)	Δn ($n_{TE} - n_{TM}$)
PMMA/PQ	1.4835	1.4844	-0.0009
PMMA/PQ/DMNA	1.4890	1.4915	-0.0025
PMMA/PQ/Zn(MA) ₂	1.4789	1.4824	-0.0035
PMMA/PQ/DMNA/Zn(MA) ₂	1.4842	1.4903	-0.0061

photopolymers doped with Zn(MA)₂ all exhibited greater birefringence than did the other photopolymers. Among them, the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer provided the greatest improvement in birefringence, presumably because the presence of Zn(MA)₂ react with the PQ and DMNA molecules to form new compounds [25–30], thereby increasing the dipole moments of the Zn(MA)₂-doped photopolymers. With a higher dipole moment led to higher birefringence by the exposed samples and increased the holographic recording characteristics.

Holographic Recording of Codoped Zn(MA)₂ Photopolymers

Figure 4 presents plots of the holographic diffraction efficiency as a function of energy. The samples of PMMA/PQ/DMNA/Zn(MA)₂, PMMA/PQ/Zn(MA)₂, and PMMA/PQ/DMNA exhibited high diffraction efficiencies, reaching maximum values of 86.2, 75.5, and 60.3%, respectively. Relative to that (36.1%) of the photopolymer doped with PQ only, we conclude that the diffraction efficiency improved significantly after codoping DMNA and Zn(MA)₂ into PMMA/PQ. For the PMMA/DMNA/Zn(MA)₂ photopolymer prepared without PQ, the diffraction efficiency was very low (ca. 1.2%). Though, Zn(MA)₂ react with DMNA to form the compounds can increased birefringence of sample [25–27]. But the Zn(MA)₂ molecule is not a photosensitive dye, that holo-

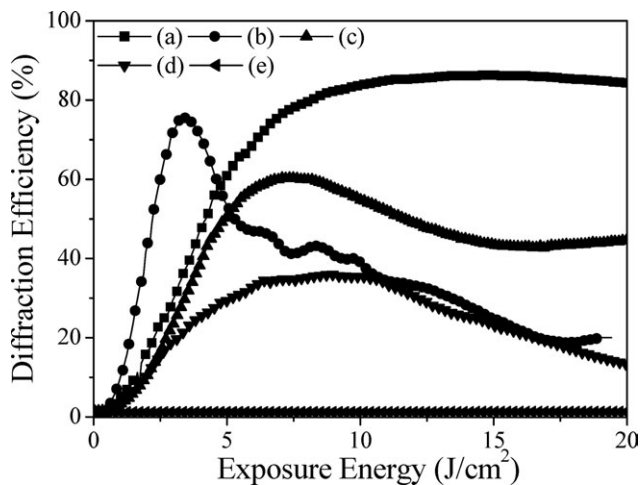


FIG. 4. Holographic diffraction efficiencies of the photopolymers (a) PMMA/PQ/DMNA/Zn(MA)₂, (b) PMMA/PQ/Zn(MA)₂, (c) PMMA/PQ/DMNA, (d) PMMA/PQ, and (e) PMMA/DMNA/Zn(MA)₂.

graphic gratings cannot be recorded in PMMA/DMNA/Zn(MA)₂ sample. This result show the holographic characteristics was mainly by the photoinduced attachment of PQ molecule to MMA and Zn(MA)₂ molecules. In which, in PMMA/PQ/DMNA/Zn(MA)₂ photopolymer the Zn(MA)₂ not only react with PQ, but also react with DMNA form other compounds, the birefringence of photopolymer was increased and improved the holographic recording characteristics, as demonstrate in Table 1.

We used perstrophic multiplexing to record 200 holograms in one location of the photopolymer. Summation of the square roots of the diffraction efficiency provided a running curve of the cumulative grating strength (Fig. 4). To obtain the holographic parameters, we performed curve fitting with the function

$$C(E) = C_{\text{sat}}[1 - \exp(-E/E_{\tau})] \quad (1)$$

where E is total exposed energy; C_{sat} (M#) is the saturation value of the curve, giving the dynamic range of the material; and E_{τ} gives the exposed energy constant of the material [8, 31]. The material sensitivity (S) is defined as an increment in cumulative grating strength with respect to the amount of exposed energy [8, 9]. When the sample is unexposed, then

$$S = dC/dE|_{E \rightarrow 0} \quad (2)$$

According to the running curve function, the sensitivity can be expressed as

$$S = C_{\text{sat}}/E_{\tau} = M\#/E_{\tau} \quad (3)$$

The values of $M\#$ and S characterize the ability of the material to be used for volume data storage [8, 9, 31].

Figure 5 displays the running curves for multiple-hologram recording in the photopolymers. After curve-fittings

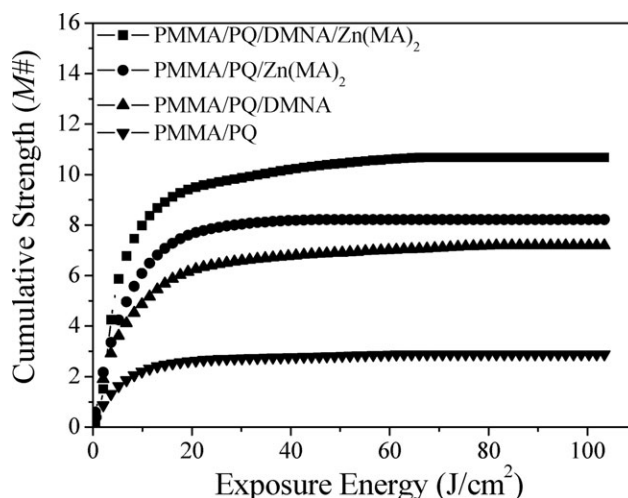


FIG. 5. Running curves for multiple-hologram recording in PMMA/PQ photopolymers doped with Zn(MA)₂ and DMNA.

TABLE 2. Dynamic range ($M\#$), exposed energy constant ($E\tau$), and material sensitivity (S) for multiplexed volume holographic recording in four photopolymers.

Sample	$M\#$	$E\tau$ (J/cm ²)	S (cm ² /J) ^a
PMMA/PQ	2.88	6.67	0.432
PMMA/PQ/DMNA	7.19	9.09	0.791
PMMA/PQ/Zn(MA) ₂	8.21	7.69	1.068
PMMA/PQ/DMNA/Zn(MA) ₂	10.68	7.58	1.409

^a $S = M\#/E\tau$.

to Fig. 5, we obtained the values of C_{sat} ($M\#$) and $E\tau$ for the various codoped photopolymers; Table 2 lists the calculated values of $M\#$ and S for each sample. The photopolymer doped with both DMNA and Zn(MA)₂ provided the highest values of $M\#$ (10.68) and S (1.409 cm²/J) among all of the samples, with greater than threefold improvements relative to those of the un-doped PMMA/PQ sample (2.88 and 0.432 cm²/J, respectively). These results are consistent with the nitroaniline modifying the holographic recording characteristics by increasing the birefringence of the photopolymer, as demonstrated in Table 1.

Chemical Characterization of Zn(MA)₂ Codoped Photopolymers

During holographic recording, PQ reaches its excited state through electron transfer and then reacts with the MMA monomer to form the photoproduct in the region

exposed to light [8, 9, 32]. The sensitivity of the hologram recording process can be improved through a modified recording mechanism after the codoping of Zn(MA)₂ into PMMA/PQ photopolymers [17, 20]. On the other hand, in this study we found that introducing DMNA into the PMMA/PQ photopolymer has the advantages of improving the recording sensitivity and dynamic range. Thus, we chemically analyzed the Zn(MA)₂ and DMNA codoped photopolymers to clarify the chemical characteristics and the mechanism of their operation. Figure 6 presents the mass spectra of each exposed sample; they provide information regarding the molecular weights of the pyrolyzed fragments of the photopolymers, allowing us to identify the possible photoproducts and deduce a plausible recording mechanism. The molecular weights of PQ, DMNA, Zn(MA)₂ and MMA are 208, 166, 235, and 100 g/mol, respectively. Figure 6a displays the mass spectrum of the pyrolyzed fragments of the PMMA/PQ photopolymer. The signal at m/z 308 corresponds to a photoproduct formed from one MMA unit and one PQ unit [8]. Figure 6b, the mass spectrum of PMMA/PQ/DMNA, also features a peak at this molecular weight, presumably representing the same compound as that in Fig. 6a. In addition, the characteristic peak of DMNA is evident at m/z 165, suggesting that DMNA does not react with either MMA or PQ to form new photoproducts in the PMMA/PQ/DMNA system after exposure to light. This observation matches the previous study [23, 25, 32, 33] was indicated that PQ molecules induce a variation in polarizability during the photoreaction process. In the PMMA/PQ/DMNA system, it is likely that the coexisting DMNA

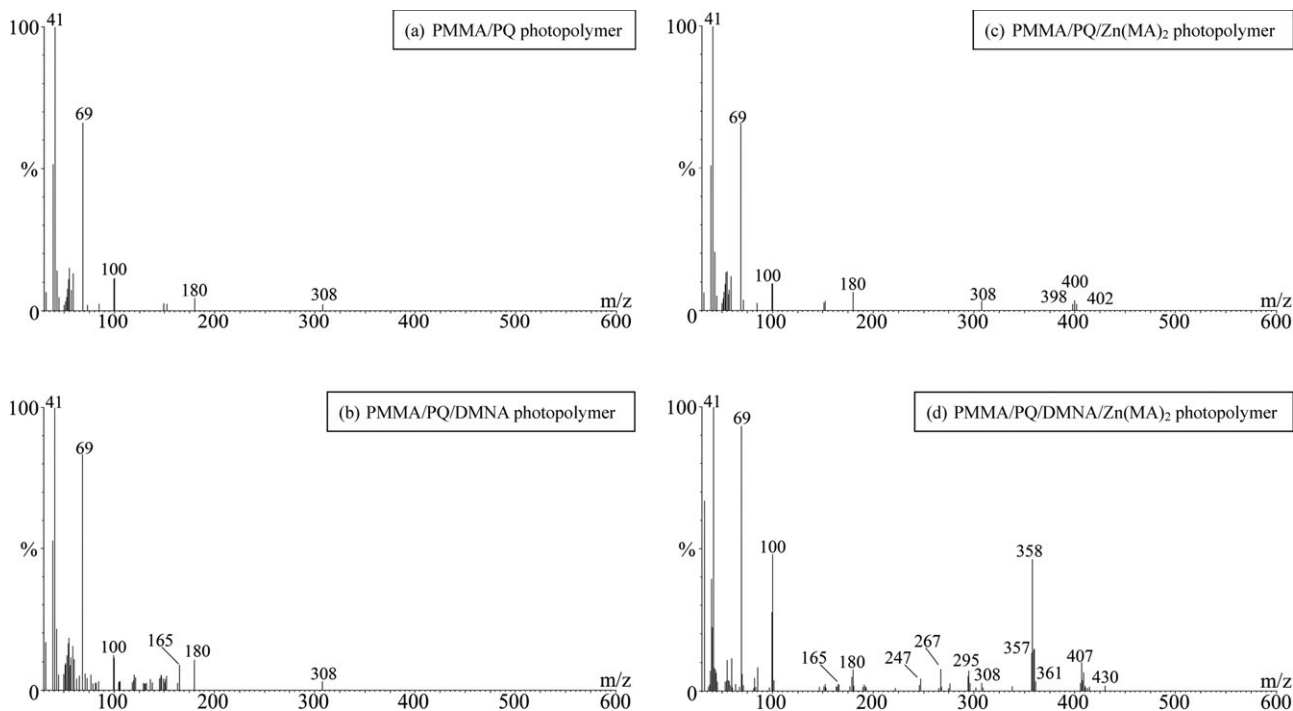


FIG. 6. Mass spectra of the light-exposed photopolymers (a) PMMA/PQ, (b) PMMA/DMNA, (c) PMMA/PQ/Zn(MA)₂, and (d) PMMA/PQ/DMNA/Zn(MA)₂.

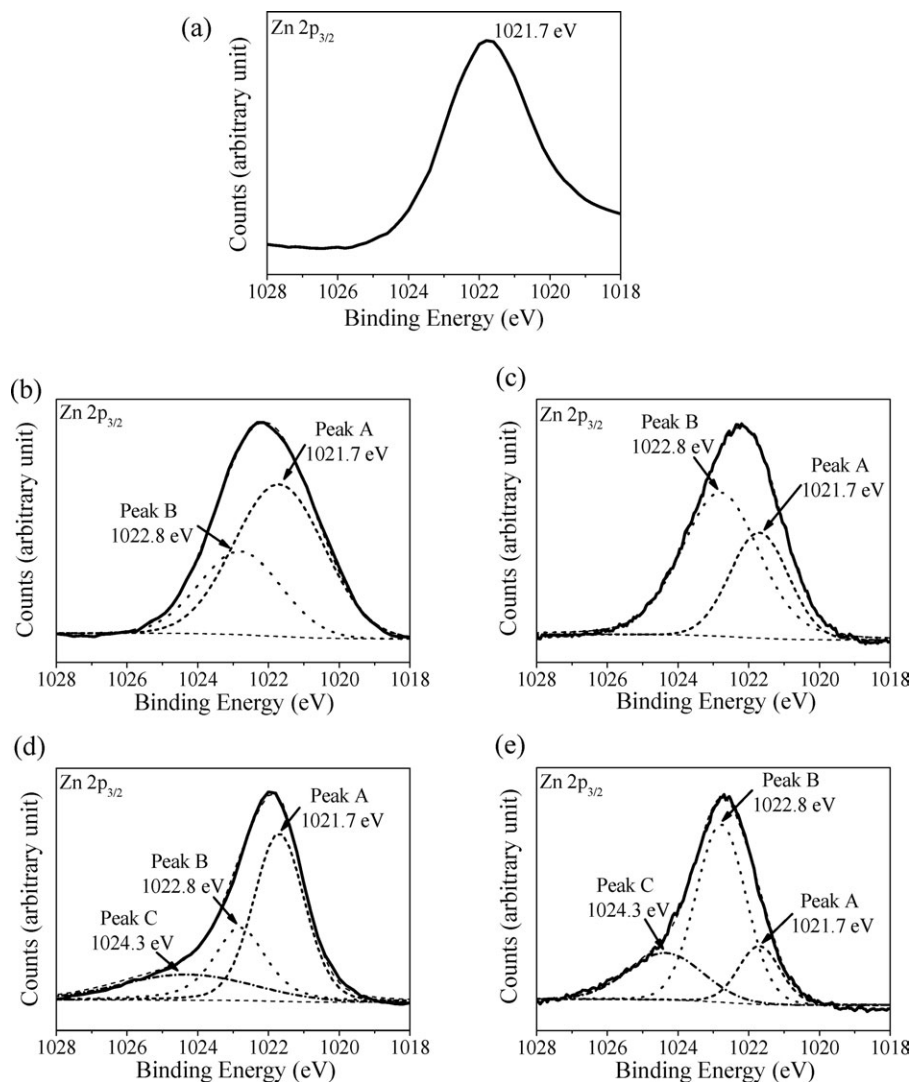


FIG. 7. Zn ($2p_{3/2}$) core level XPS spectra of (a) standard $\text{Zn}(\text{MA})_2$, (b) unexposed $\text{PMMA}/\text{PQ}/\text{Zn}(\text{MA})_2$, (c) exposed $\text{PMMA}/\text{PQ}/\text{Zn}(\text{MA})_2$, (d) unexposed $\text{PMMA}/\text{PQ}/\text{DMNA}/\text{Zn}(\text{MA})_2$, and (e) exposed $\text{PMMA}/\text{PQ}/\text{DMNA}/\text{Zn}(\text{MA})_2$.

molecules affected the polarizability of PQ during the recording process [23], such that the photoproducts were formed with a more-planar molecular orientation to improve the holographic data storage characteristics. Figure 6c presents the mass spectrum of the $\text{PMMA}/\text{PQ}/\text{Zn}(\text{MA})_2$ photopolymer; again, the peak at m/z 308 is present, in addition to other peaks in the range m/z 398–402, which presumably arose from the fragmentation of $\text{Zn}(\text{MA})_2$ and further reactions with PQ. The decomposition of $\text{Zn}(\text{MA})_2$ could involve the loss of one MA molecule, with which a PQ molecule might react to form a new photoproduct. The mass spectrum of the $\text{PMMA}/\text{PQ}/\text{DMNA}/\text{Zn}(\text{MA})_2$ photopolymer (Fig. 6d) reveals the existence of signals at m/z 295–296 and 308, representing the product formed from one MMA unit and one PQ unit [8]. In which, the peaks at m/z 406–430 was likely the result in Fig. 6c. We attribute the peaks at m/z 357–361 to a molecule comprising one ZnMA unit and one PQ unit.

The peaks in the molecular weight range m/z 267–286; however, might be due to the fragmentation of one ZnMA molecule attached to a NO_2 functional group [25–27], which presumably detached from DMNA [25–26, 34]. It means that ZnMA interaction with DMNA. The compounds had higher dipole moments and let to higher birefringence by the photopolymers and increased the holographic recording characteristics, it was demonstrated in Fig. 5.

To identify the recording mechanism, we used X-ray photoelectron spectroscopy (XPS) to measure the Zn ($2p_{3/2}$) energy levels as a means of characterizing the chemical compositions of the zinc elements in the photopolymers. Figure 7 displays the Zn ($2p_{3/2}$) XPS spectra of the $\text{PMMA}/\text{PQ}/\text{Zn}(\text{MA})_2$ and $\text{PMMA}/\text{PQ}/\text{DMNA}/\text{Zn}(\text{MA})_2$ photopolymers, with Gaussian deconvolution of the overlapping peaks. In Fig. 7a, the standard $\text{Zn}(\text{MA})_2$ XPS spectrum of Zn ($2p_{3/2}$), the signal of the free Zn ($2p_{3/2}$) is

TABLE 3. Atomic percentages of zinc atoms in various states in the unexposed and exposed photopolymers PMMA/PQ/Zn(MA)₂ and PMMA/PQ/DMNA/Zn(MA)₂ (calculated from XPS data using the Shirley method).

Zn states	Zn atomic %			
	PMMA/PQ/Zn(MA) ₂		PMMA/PQ/DMNA/ Zn(MA) ₂	
	Unexposed	Exposed	Unexposed	Exposed
State A ^a	66.7	33.6	53.1	16.7
State B ^b	33.3	66.4	27.3	60
State C ^c	–	–	19.6	23.3
Peak A ratio ^d	1.985		3.180	

^a State A: free Zn, as in Zn(MA)₂.

^b State B: Zn interacts with PQ.

^c State C: Zn interacts with DMNA.

^d Peak A ratio = [unexposed peak A (%) / exposed peak A (%)].

located 1021.7 eV. The XPS spectrum of the unexposed PMMA/PQ/Zn(MA)₂ photopolymer (Fig. 7b) reveals a peak A (Zn at state A) at 1021.7 eV, which we attribute to free Zn(MA)₂, and a peak B (Zn at state B) at 1022.8 eV, which we attribute to the photoproduct formed from Zn(MA)₂ interacting with PQ. The XPS signals of the exposed PMMA/PQ/Zn(MA)₂ photopolymer (Fig. 7c) were similar to those in Fig. 7b, but the area ratio (B/A) of the two peaks was different. Prior to exposure, the B/A peak area ratio was 33.3/66.7, suggesting that one-third of the Zn species had already interacted with PQ units. After exposure, the peak area ratio was 66.4/33.6, meaning that two-thirds of the Zn species had interacted with PQ moieties. Figure 7d displays the Zn (2p_{3/2}) XPS spectrum of the unexposed PMMA/PQ/DMNA/Zn(MA)₂ photopolymer; we ascribe the peaks at 1021.7 (peak A), 1022.8 (peak B), and 1024.3 (peak C) eV to free Zn(MA)₂ (state A), Zn(MA)₂ having interacted with PQ (state B), and Zn(MA)₂ having interacted with DMNA (state C), respectively. The peak locations in the XPS spectrum of the exposed PMMA/PQ/DMNA/Zn(MA)₂ photopolymer (Fig. 7e) were similar to those in Fig. 7d. The results can be further identified through calculating the area of peak. For all of the light-exposed samples, the area of peak A decreased while that of peak B increased significantly, presumably because of the formation of a photoproduct from Zn(MA)₂ and PQ after exposure to light. The area of peak C increased slightly, revealing that Zn(MA)₂ interacted primarily with PQ and to a much lesser extent with DMNA, in agreement with the conclusions drawn from the mass spectra. This result show the main effect of the holographic recording characteristics was the PQ react with MMA and Zn(MA)₂ molecules, as demonstrate in Fig. 4. Table 3 lists the peak A ratios (the area of peak A of the unexposed photopolymer divided by that of the exposed sample) of all of the samples. Through the variations of the peak A ratios, we can determine the degrees of reaction of the Zn(MA)₂ species. The peak A ratios of

the PMMA/PQ/Zn(MA)₂ and PMMA/PQ/DMNA/Zn(MA)₂ photopolymers were 1.985 and 3.180, respectively; the higher value of the latter implies that more Zn(MA)₂ molecules reacted with PQ and DMNA to form new compounds during light exposure. In which, the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer had greatest birefringence than other photopolymers. At the same time, the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer also exhibited superior holographic recording characteristics, as revealed in Fig. 5. Hence, the performance of the diffraction efficiency, M#, and the material sensitivity were correlated to the degrees of photoreaction in the samples. Together, our results indicate that the performance of the PMMA/PQ photopolymer can be enhanced by the presence of Zn(MA)₂ and DMNA in the system.

CONCLUSIONS

The holographic data storage characteristics of PMMA/PQ photopolymers are significantly enhanced after introducing Zn(MA)₂ and DMNA. The results of single-hologram recording revealed that the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer provided a diffraction efficiency higher than those of the other tested photopolymers. Furthermore, in multiple-hologram recording tests, the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer displayed the highest value of M# and sensitivity. The values of η_{\max} and M# improved by 2.39 and 3.69 times, respectively, when Zn(MA)₂ and DMNA were codoped into the photopolymer. Using MS and XPS to investigate the effects of Zn(MA)₂ and DMNA on the holographic storage characteristics, we found that some of the PQ and DMNA molecules bound to Zn(MA)₂ in the PMMA/PQ/DMNA/Zn(MA)₂ photopolymer. Our results indicate that the PMMA/PQ photopolymer can display superior holographic recording characteristics after codoping with organometallic and nitroaniline compounds [namely Zn(MA)₂ and DMNA, respectively] to further promote the PQ photoreaction and birefringence.

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