

Fabrication and characterization of poly(methyl methacrylate) photopolymer doped with 9,10-phenanthrenequinone (PQ) based derivatives for volume holographic data storage

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Abstract

We present our studies on the photopolymer of poly(methyl methacrylate) (PMMA) doped with 9,10-phenanthrenequinone based derivatives for volume holographic storage. By introducing different functional groups on the side-chain of 9,10-phenanthrenequinone molecule, the holographic characteristics of the material can be modified. The photoreaction involved with the holographic recording in the samples was investigated by measuring UV–Vis absorption spectrum and mass spectrum. The experimental results show that the similar behaviors were exhibited in these photopolymers. It is found that phase hologram recording in our PQ derivatives doped PMMA photopolymer involves a structure change of the quinone based molecule, which induces a strong change of the refractive index. Experimental characterizations on holographic data storage, including material sensitivity, dynamic range ($M\#$) and bit-error-rate have been performed. We found that, by selecting appropriate functional groups, an improvement in sensitivity and $M\#$ for holographic data storage can be achieved.

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1. Introduction

Recently, many experimental works have demonstrated that polymer-based recording materials are very attractive for the holographic recording applications [1–6]. Photopolymer materials can provide large modulation in refractive index, and they are easy to fabricate because dedicated crystal growth facilities are not required. In contrast, photopolymer materials also possess some disadvantages. Among them, the problem of material shrinkage induced by light exposure is the most serious. This effect induces dimensional distortions on the recorded gratings such that

the Bragg conditions for these volume holograms are missed and the recorded information cannot be retrieved completely [7,8]. Shrinkage effect is to some extent in proportional to the material thickness. Therefore, conventional photopolymerizable material is limited to hundreds μm .

In our group, we have adapted the doped system to produce photopolymer and developed a technique for synthesizing the 9,10-phenanthrenequinone-doped poly(methyl methacrylate) (PQ/PMMA) photopolymer with a few mm thick. The experimental results demonstrated that PQ/PMMA photopolymers possess not only high optical quality but also negligible shrinkage effect under light exposure, thus they are suitable for the volume holographic recording [9–11]. Our strategy to alleviate the shrinkage

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problem is to separate the photochemical reaction during holographic recording from polymerization of host monomer molecules during material preparation, since most of shrinkage of material occurs at polymerization of recording elements. This can be achieved if most of the MMA molecules are polymerized to form a host polymer matrix PMMA during material preparation in a way that only a few percentages of un-reacted MMA monomer molecules are left and dispersed in the polymer matrix. The monomer molecules together with the doped photosensitive element, PQ molecules, are responsible for holographic recording. Our previous investigations have demonstrated the successful fabrication of this doped polymer system. However, the recording sensitivity and the dynamic range ($M\#$) are still needed to be improved.

In order to improve the material, chemical analyses have been performed to investigate the physical mechanism of holographic recording on PQ/PMMA photopolymer. It was found that the photochemical process in our PQ/PMMA sample is a one-to-one photoreaction [12]. That is, the *o*-quinone double bond on the carbonyl functional group of the PQ molecule reacts with the carbon double bond on vinyl group of the residual MMA monomer. The photo-produced compound is less conjugated than the original molecular structure of PQ, such that the refractive index of the sample has been changed. As the results, a difference in the refractive index between bright and dark areas, following to that of the interference pattern, has formed and which is responsible for phase grating recording. Since such photoreaction does not involve with the backbone of the polymer matrix, hence the holographic recording induces very little influence on the matrix structure of PMMA chains. Thus, volume shrinkage due to photo-polymerization, which always happens in conventional photopolymer materials, can be minimized.

Above information about the process of photoreaction provide some hints for improving the PMMA photopolymer. Since the photoreaction between PQ and MMA molecules play an important role of holographic recording, hence modification of PQ molecules may be able to enhance the optical sensitivity and dynamic range for recording. In this paper, we replace the PQ molecules by doping different 9,10-phenanthrenequinone based derivatives, all with *o*-quinone double bonds. We hoped that, by doping photosensitive molecules with different side link functional groups, including electron-donor, electron-withdrawing, and aromatic structure, around the *o*-quinone bond of the molecule, it is possible to modify photo-induced properties of photosensitive elements and then modify the holographic characteristics of materials. Four different 9,10-phenanthrenequinone (PQ) based derivatives are used to fabricate new volume holographic photopolymers. The holographic recording characteristics of the different samples are studied and discussed. The results show that doping photosensitive molecule with electron-donor type can improve not only dynamic range but also sensitivity of the photopolymer material.

2. Experiment descriptions

2.1. Material components and sample fabrication

The monomer, methyl methacrylate (MMA) was distilled under low pressure to remove inhibitor after purchasing from Sigma Aldrich [13]. In addition to 9,10-phenanthrenequinone (PQ), three kinds of PQ-based derivatives are chosen as photosensitive molecules: 1-isopropyl-7-methyl-9,10-phenanthrenequinone (named as PQ1), 2-nitro phenanthrenequinone (named as PQ2) and 11,12-dihydrochrysen-11,12-dione (named as PQ3). The azoisobutyronitrile (AIBN), thermo-initiator, was purified through recrystallization before used. Fig. 1 shows the molecular structure of each component. It can be seen that PQ1 molecule has additional isopropyl and methyl side groups, which serve as an electron-donor functional group. Under light illumination, these groups can provide additional electrons to stabilize radical structure of the molecule such that its activation energy of molecule can be decreased. According to kinetics of chemical reactions based on the stability of intermediates [14], the photoreaction of PQ1 and MMA can be speed up. PQ2 molecule has an additional nitro group, which usually performs a function of electron-withdrawing. With this group, the activation energy of the molecule increases such that the molecule may not easily turn into a radical under light illumination. However, the nitro side group usually induce large refractive index birefringence and so the strength of holographic recording can be enhanced. PQ3 molecule has an additional aromatic structure, which increases conjugate length of the molecule. With longer conjugate length, the refractive index change can be increased under light illumination.

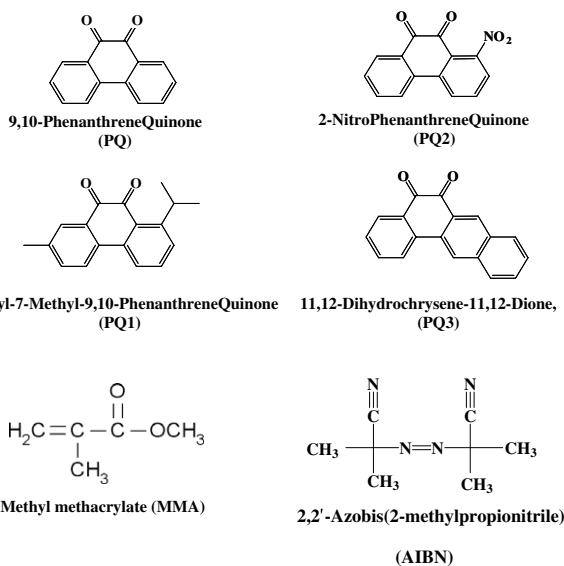


Fig. 1. Chemical structures of elements for our poly(methyl methacrylate) (PMMA) photopolymer doped with different quinone-based molecules: MMA, AIBN, PQ and its derivatives (PQ, PQ1, PQ2 and PQ3).

Four different samples were fabricated. Each was doped with different molecules: PQ, PQ1, PQ2, and PQ3. During fabrication, for each sample, one of the photosensitive dyes together with the AIBN molecules (1% by weight) was dissolved into the purified MMA solution. We then utilized a two-stage method to synthesize our bulk samples. In the first stage, the solution was stirred at 30 °C for around 60 h until the solution turned to high viscosity. In the second stage, the viscous solution was then poured into the glass cell with dimensions of 10 cm × 10 cm and thickness of 2 mm, and baked at 45 °C for 3 days. This two-step procedure polymerized most of MMA molecules and was found to obtain bulk samples with good optical quality. The sample was then removed from the container to be used for experiments. Our samples appear to be yellowish color, with a clear optical transmission. In order to study the effect of photosensitizer, two sets of samples with different doping concentrations of photosensitizer were prepared. One set of samples was fabricated with the same molar concentration (ca. 155 μmol), the other set was fabricated with the saturated concentration. The doping concentrations of different samples are listed in Table 2. This set of samples was used to test the capability of different materials for holographic data storage.

2.2. Photochemical measurements

To identify photoreactions in our photopolymer samples, we have performed two measurements on the samples with two different states: unexposed and exposed states. The unexposed state is the sample as fabricated. To reach the exposed state, the sample was illuminated by a 514 nm argon laser with intensity of 3 W/cm² until it changes from yellow to transparent. First, UV–Vis spectra of the exposed and unexposed states of sample were measured by using a Hitachi-U2000. This tells us the range of sensitive wavelengths of the samples. It can also be used to observe the occurrence of the conjugation structure change of the chemical compounds. Secondly, mass spectra of the samples were measured by using a VG Biotech TRIO-2000. The results provide the molecular weight distribution of the compounds in the exposed and unexposed states of the sample, which will tell us if there is any new compound produced by light exposure.

2.3. Holographic characteristics measurement

A typical optical setup for holographic data storage has been applied. The plan wave light at 514 nm was split into two beams with intensity ratio at 1:1, which were incident into the sample symmetrically with an intersection angle of 30° outside the sample. For multiple recording at one spot of the sample, peristrophical multiplexing technique was applied by rotating the sample. Two-hundred holograms were recorded in one location, with 125 mW/cm² and 5 s exposure time for each recording. We monitored the diffraction efficiency of the gratings after each record-

ing. 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. The summation of the root square of the diffraction efficiency of the current hologram with that of previously recorded form a running curve of the cumulative grating strength. The running curve is plotted as a function of total exposure energy that has been illuminated on the material during recording. By curve-fitting with the function: $C(E) = C_{\text{sat}}[1 - \exp(-E/E_{\tau})]$, where E is the total exposure energy, the dynamic range of material can be found to be the saturation value C_{sat} (known as value of $M\#$ [15]), and E_{τ} gives the exposure energy constant of the material. We define the material sensitivity (S) to be the increment in cumulative grating strength with respect to the amount of exposure in a short period when the sample is fresh, $S = dC/dE|_{E \rightarrow 0}$. According to the running curve, S can be written as: $S = C_{\text{sat}}/E_{\tau} = M\#/E_{\tau}$. By estimating and comparing the $M\#$ and S of different PQ-based derivatives doped PMMA photopolymer samples, we can investigate the effect of photosensitive molecules on the holographic recording characteristics of the photopolymer materials.

3. Results and discussion

3.1. Photochemical measurements

3.1.1. UV–Vis spectra measurements

Typical optical absorption spectra of our samples are shown in Fig. 2. It can be seen that in Fig. 2a, the unexposed samples possess strong absorption below the blue wavelength (<450 nm), and they are transparent for wavelengths longer than 540 nm. At 514 nm wavelength, the absorption coefficients are 1.94 cm⁻¹, 2.42 cm⁻¹, 0.48 cm⁻¹ and 0.88 cm⁻¹ for PQ, PQ1, PQ2 and PQ3 doped PMMA samples, respectively. The results show that 514 nm wavelength is suitable for holographic recording in these samples.

For the exposed samples, the absorption band shows a blue shift, as illustrated in Fig. 2b, with an absorption band in the UV regime (<400 nm). The strong blue shift implies that the photoproducts become less conjugated than those of the un-exposed PQ-based derivatives. As demonstrated in our studies on PQ/PMMA sample [12], this kind of molecular structure change is the main effect to produce refractive index change for holographic recording in the sample.

3.1.2. Mass spectra measurements

Fig. 3a–c shows the mass spectra of unexposed and exposed samples of PQ1/PMMA, PQ2/PMMA, and PQ3/PMMA, respectively. They all show an important behavior that in the exposed samples new peak signals appear at higher molecular weight region (ca. ~360), which is a characteristic difference between the photo-exposed and unexposed states of the samples. Since the molecular weights of PQ1, PQ2, PQ3 and MMA are 264, 253, 258

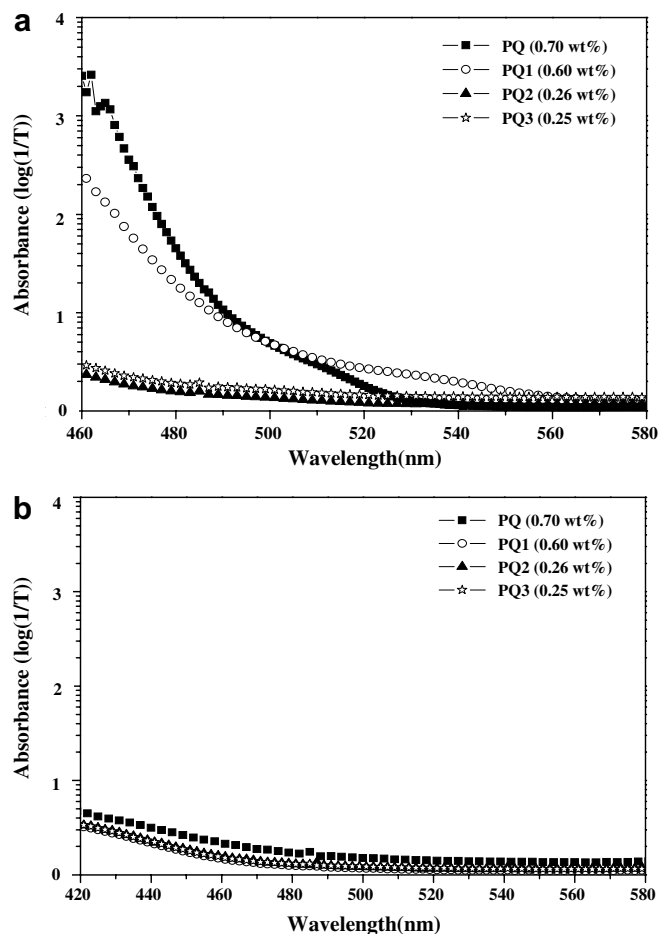


Fig. 2. UV-Vis absorption spectra of PMMA samples doped with saturation concentrations of different quinone-based molecules (a) unexposed and (b) exposed states of the samples. (All the samples with the thickness of 2 mm and the saturation doping concentration of PQ derivatives).

and 100, respectively, the existence of peak signals at molecular weight of 364, 353, and 369, respectively, is evidence that the photoproduct is one MMA molecule attached to one PQ derivatives molecule in our photopolymer samples. Note that the new peak at molecular weight of 369 for the exposed PQ3/PMMA sample is deviated by eleven from that of 358 as we supposed. The additional molecular weight might be attributed to the photoproduct protonated with eleven hydrogen atoms.

The above result reveals an important characteristic of light exposure for the PQ1/PMMA, PQ2/PMMA and PQ3/PMMA samples, i.e., the new compound produced by the photo-exposed is a photoproduct of one PQ derivatives molecule (PQ1, PQ2 and PQ3) attached to one MMA molecule. This kind of photo-chemical reaction is similar to that of PQ/PMMA photopolymers. Since the backbone structure of PMMA is not involved in the photo-chemical reaction for optical exposure, hence negligible shrinkage effects could be achieved under light exposure. Thus, we may anticipate that this dye doped PMMA photopolymer

system will maintain the negligible shrinkage effect during holographic exposure. And, this will facilitate multiplexed volume recording in holographic data storage.

3.2. Holographic recording

Fig. 4a shows the running curve of the cumulative grating strength of the un-exposed samples, which are doping with the same molar concentrations. Using curve-fitting and the formulas, described in Section 2.3, the $M/\#$, E_r , and S are estimated and listed in Table 1. It is seen that PQ2/PMMA sample possesses a slightly larger $M/\#$ than that of PQ/PMMA sample (from 0.66 to 0.76), whereas the sensitivity is only 63% of that of PQ/PMMA sample. On the other hand, the $M/\#$ of PQ1/PMMA sample is reduced to 83% of that of PQ/PMMA sample, whereas the sensitivity has been improved by three times. These two results followed the expectation if we consider how the PQ-based derivatives modify the photo-chemical reaction of holographic recording. The aliphilic (R-) electron-donor group on PQ1 molecule plays an electron-donor such that it accelerates the photoreaction and hence the recording sensitivity is increased. As for PQ2, the nitro (NO_2 -) electron-withdrawing group on PQ2 makes the electron diffusely distributed and will decelerate the photoreaction, thus the speed of photoreaction has been slowed down. On the other hand, the nitro group increases the birefringence effect of sample such that the dynamic range of the sample is increased.

Originally, we consider the aromatic structures of PQ3 molecules to form larger photocompound under light illumination, which will produce the largest changes of refractive index. Mass spectra measurement of new peaks at molecular weight of 369 confirms our expectation. Nevertheless, holographic experimental results show that the $M/\#$ of PQ3/PMMA sample is reduced by 65% of that of PQ/PMMA sample, and sensitivity of material is the worst in all of samples. The reason for this inconsistency between the photochemical reaction and holographic measurement is still to be investigated.

In fact, different molecular structures of quinone-based molecules possess different solubility in PMMA matrix. In order to further enhance the photochemical reaction of the photopolymer, we fabricated samples with saturation concentrations of photosensitizers. The holographic characteristics of the samples were measured by using the same optical setup, and the results are shown in Fig. 4b. From this figure the material characteristics are estimated and listed in Table 2. It is seen that, under these concentrations, the PQ1/PMMA sample is the best one among the four samples. The sensitivity is 4.4 times faster than that of PQ/PMMA, and the $M/\#$ is increased from 3.23 to 5.18. The results show that by selecting appropriate PQ-based derivative molecules with suitable concentration, an improvement in recording sensitivity and dynamic range of samples can be achieved.

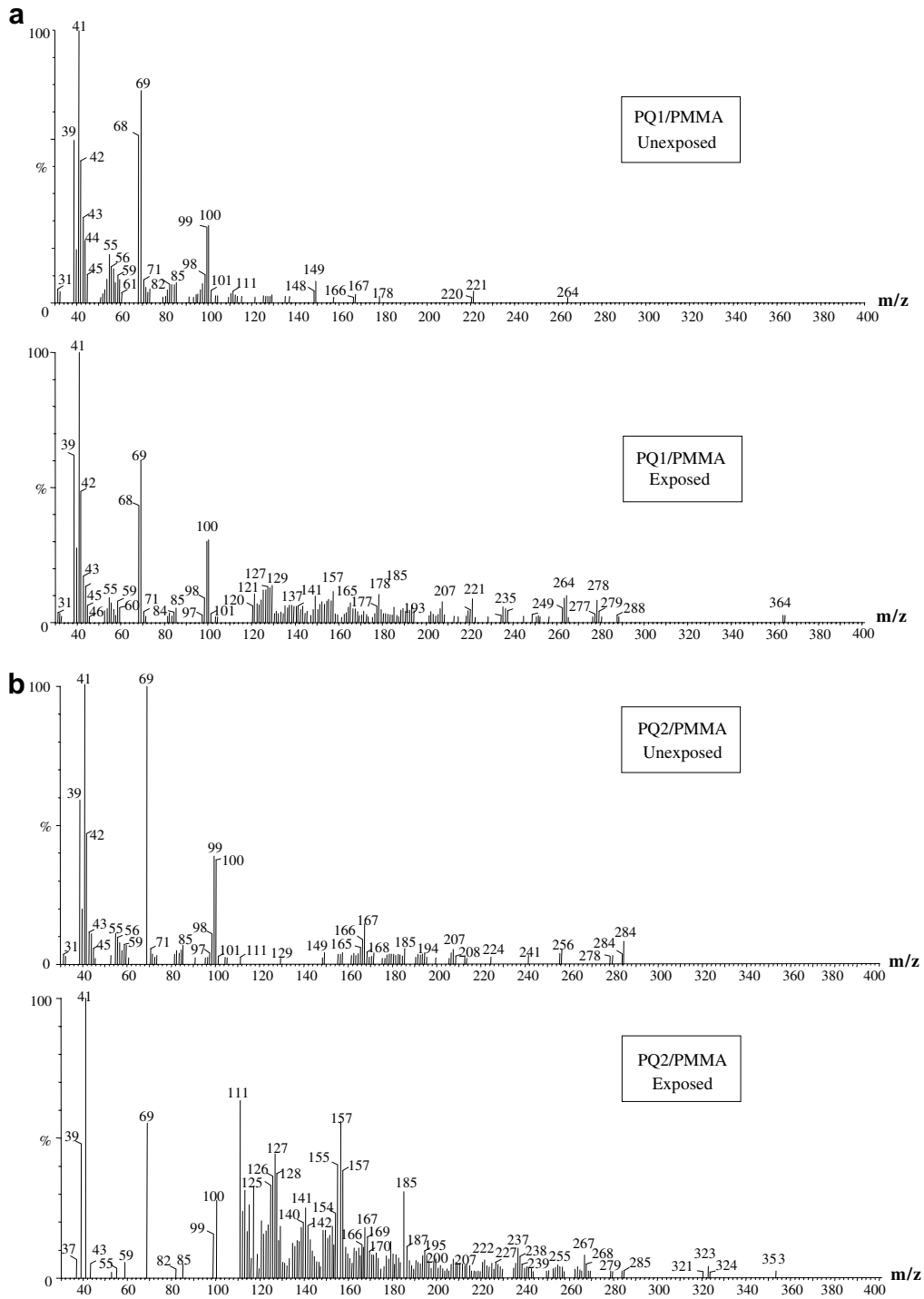


Fig. 3. The mass spectra of unexposed and exposed states of (a) PQ1/PMMA sample, (b) PQ2/PMMA sample, and (c) PQ3/PMMA sample.

4. Characterize PQ1/PMMA sample for holographic data storage

Since PQ1/PMMA photopolymer is the best one among the four samples, we performed further experiments on this sample for holographic data storage application. First, we recorded a plane-wave hologram in the sample with different thickness, and then measured the Bragg selectivity of

the recorded grating. Fig. 5 shows the experimental results, in which the diffracted power of the grating is plotted as a function of the angular deviation for 1.2 mm and 2.4 mm thick samples, respectively. It can be seen that two curves show several clear minima points as the angular deviation reaches sinc nulls, which is a typical phenomenon observed in a Bragg grating. In addition, the maximal diffracted power of each curve occurs at zero angular deviation,

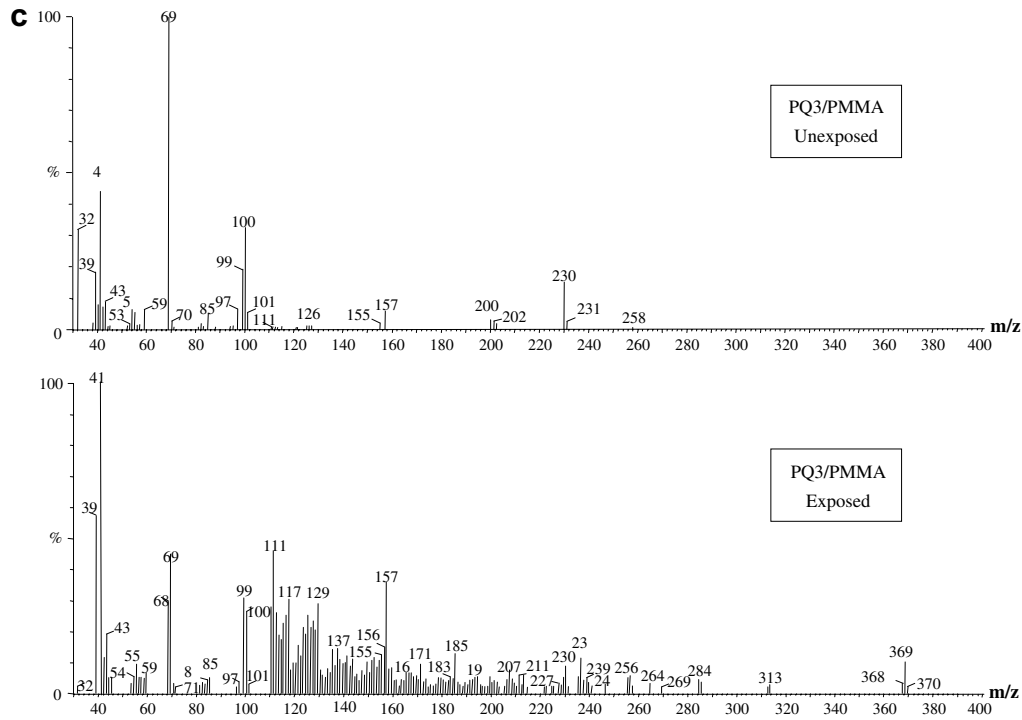


Fig. 3 (continued)

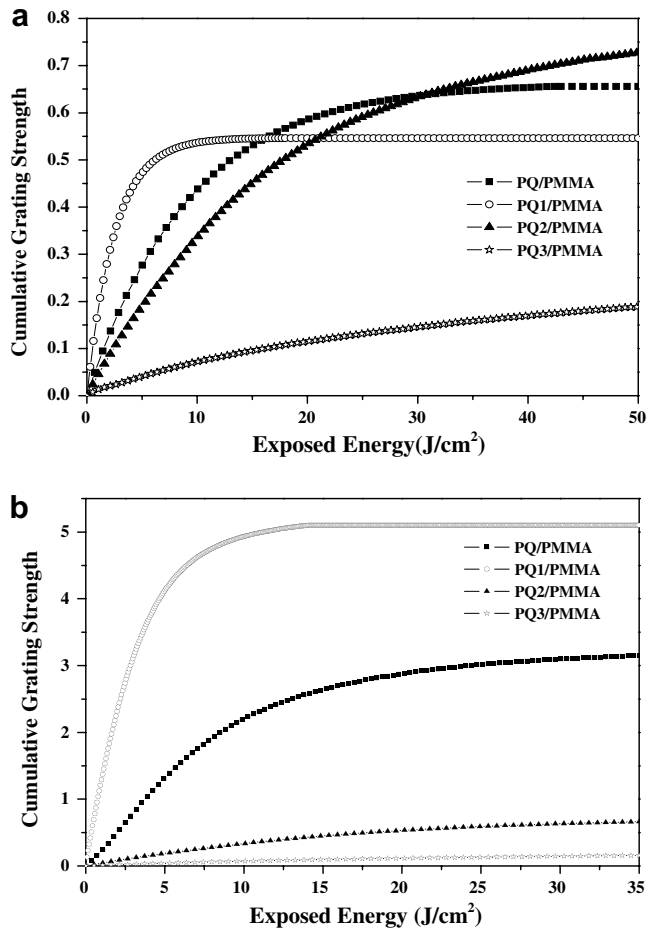


Fig. 4. Running curves of multiple-hologram recording in PMMA photopolymer doped with different quinone-based molecules (PQ, PQ1, PQ2, and PQ3): (a) same molar concentrations, and (b) saturation concentrations.

Table 1

Characteristics of multiplexed volume holographic recording in quinone-based photopolymers with same molar photosensitizer concentrations: $M/\#$ (dynamic range), E_τ (characteristic exposure energy constant), S (material sensitivity)

	PQ	PQ1	PQ2	PQ3
Conc (wt.%)	0.202	0.256	0.245	0.25
$M/\#$	0.66	0.55	0.76	0.22
E_τ (J/cm ²)	9.3	2.52	17.13	26.9
S (cm ² /J)	0.07	0.22	0.044	8×10^{-3}

Table 2

Characteristics of multiplexed volume holographic recording in quinone-based photopolymers with saturation photosensitizer concentrations: $M/\#$ (dynamic range), E_τ (characteristic exposure energy constant), S (material sensitivity)

	PQ	PQ1	PQ2	PQ3
Conc (wt.%)	0.7	0.7	0.26	0.25
$M/\#$	3.23	5.18	0.82	0.22
E_τ (J/cm ²)	9.07	3.23	17.5	26.9
S (cm ² /J)	0.36	1.6	0.047	8×10^{-3}

which corresponds to the original writing angle of the reference beam. This indicates that the material shrinkage of our PQ1/PMMA sample is so small to be negligible, and thus this material is suitable for volume holographic applications.

Next, image quality of the holographic recording in PQ1/PMMA sample was tested. We recorded a Fresnel hologram by using a picture of randomly distributed binary data (0 and 1) as an object image, in which the sample is placed near the Fourier plane of the imaging lens. In

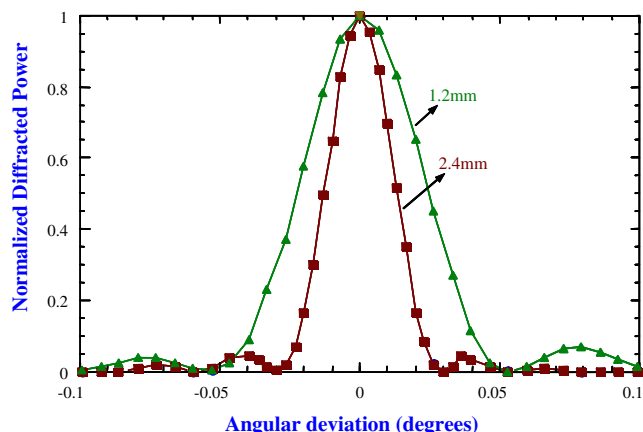


Fig. 5. The diffraction power of a plane grating as a function of the angular deviation for 1.2 mm and 2.4 mm thick PQ1/PMMA samples.

experiments, we used a CCD camera with auto gain control function to capture the reconstructed image. Fig. 6a shows photograph of the directly transmitted image and the reconstructed image with diffraction efficiency of $\sim 10^{-4}$. It can be seen that the reconstructed image retains clear fidelity. The distortion of the image and scattering background noise are not obvious. The statistic distribution of

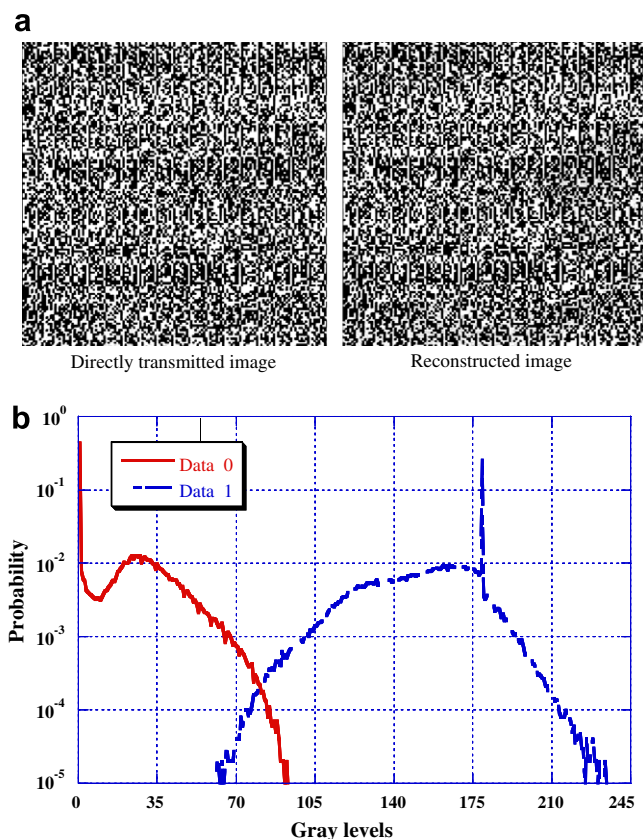


Fig. 6. The testing of the image quality of the holographic recording in PQ1/PMMA sample: (a) the reconstructed randomly distributed binary picture with diffraction efficiency of $\sim 10^{-4}$, (b) the statistic distribution of gray level of each pixel on the reconstructed image.

the grey levels for the reconstructed image is shown in Fig. 6b. It can be seen that the signal curves corresponding to input pixels of data 0 can be fairly separated with that of data 1. If we choose the threshold for separating data 1 from data 0 to be at the cross-point of the two curve. In this case, it is at grey level of 80. Then, the error bits can be calculated by counting the number of data 0 bits with grey levels above the threshold, and vice versa for the data 1 bits with grey levels below the threshold. The bit-error-rate is obtained by dividing the number of error bits by the total number of pixels, which is around 1.8×10^{-4} . This is a raw bit-error-rate, is good enough for the application of volume holographic storage. For comparison, we use the same method to evaluate the directly transmitted image. No error bit is found when the optical setup has been aligned well. It indicates that the scattering noise produced from our material can be neglected. Thus, the error bits on the reconstructed image occur primarily because of non-uniform and weak diffraction from hologram, such that we anticipate bit-error-rate can be improved by increasing diffraction efficiency. On the other hand, in this aspect, since material scattering comes from non-homogeneity of the refractive index, our technique of pre-polymerization during material fabrication seems to produce satisfactory uniformity of refractive index for holographic storage in PQ1/PMMA photopolymer sample.

5. Conclusions

We have fabricated four kinds of doped PMMA photopolymers by using different PQ-based derivative molecules. The optical exposure and holographic characteristics of the samples have been measured and compared. Experimental results show that by selecting suitable functional group on photosensitive molecules with suitable doping concentrations, holographic recording properties of photopolymers can be improved. The best one among the four samples is PQ1/PMMA photopolymer, which possesses the performances of the $M\#$ around 5.18 and the recording sensitivity to be $1.6 \text{ cm}^2/\text{J}$. The results indicated that electron-donor group is the most efficient accelerator for improving holographic recording characteristics of the recording materials. In addition, the experimental characterizations on PQ1/PMMA samples have shown that the doped system is good strategy to produce photopolymer with good optical quality and minimized material shrinkage which makes our photopolymer material is particularly useful for holographic data storage applications.

Acknowledgements

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