Experimental characterization of phenanthrenequinone-doped poly(methyl methacrylate) photopolymer for volume holographic storage

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1 Introduction
Holographic data storage has been considered as one of the next-generation information storage technologies because of its large storage capacity and fast data access. By using a suitable multiplexing scheme, thousands of pages of optical information can be recorded onto one location of a recording medium. The recorded information can then be read out in a page format with ultrahigh data rate. Holographic data storage systems with large storage capacity, high data readout rate, good image quality, and low bit error rate have been proposed and demonstrated.1,2

The main components necessary for this technology are optical spatial light modulators (SLMs), a detector array, and a holographic recording medium. The first two are the interface devices for optical data input and output. In recent years, rapid advances in liquid-crystal displays (LCDs) and charge-coupled devices (CCDs) have yielded high-quality input and output devices that are capable of operating at one million bits per frame. However, lack of a suitable recording material still obstructs further development of holographic data storage. Recently, many experiments have demonstrated the feasibility of using polymer-based materials for holographic data storage.1,3-9

For a good holographic recording material, many characteristics are required, such as high optical sensitivity, a simple development procedure, uniform spatial-frequency response, large diffraction efficiency, high optical quality, and long-term stability. For volume holographic storage using thick materials, good dimensional stability is the most characteristic requirement. It has been shown that a few percent of dimensional change in the recording material during (or after) holographic recording will result in a loss of Bragg condition such that the recorded information cannot be read out completely. The thicker the material, the more serious the shrinkage effect.10-12 As a result, typical photopolymer holographic materials are limited to a few millimeters in thickness.

To alleviate the shrinkage effect in thick materials, some techniques for fabricating photopolymer materials have been proposed and demonstrated.10,13-16 Among these recording materials, poly(methyl methacrylate) (PMMA) is one of the most popular polymer bases for the binder, due to its good dimensional stability and good optical quality. Recent research has shown that PMMA doped with phenanthrenequinone (PQ) could be very attractive for volume holographic recording because it is easy to form in bulk with negligible photochemically induced dimensional change and good optical quality.7,13-16

In this paper, we present our experimental investigations into bulk PQ-doped PMMA. In Sec. 2, we describe the design strategy and the procedure for making thick polymer samples with good optical quality. Then, in Sec. 3, we investigate the optical characteristics of the material. In Sec. 4, we present the holographic characteristics of the samples for multiple hologram storage. The coefficient in the dependence of diffraction efficiency on number of holograms is measured, and exposure schedules for achieving uniform diffraction efficiency are presented. In Sec. 5, multiple storage and reconstruction of 250 holograms in a 1×1×1-cm³ cube is demonstrated experimentally. Finally, some conclusions are given in Sec. 6.

2 Material Preparation
We first describe our strategy for making bulk samples of PQ:PMMA. The aim is to make a thick photopolymer material that undergoes minimal dimensional shrinkage during holographic recording. Typical photopolymer materials consist of a photopolymerizable monomer, a photoinitiator, and a sensitizer in a polymer binder.3-5 During the optical
exposure, incident photons initiate a chain reaction of photopolymerizable monomer molecules, which causes a strong change of the refractive index of the photopolymer such that a phase hologram is formed. In these conventional photopolymer materials, a large number of monomer molecules are involved in the formation of the hologram. As a result, the materials exhibit significant changes in both the geometrical dimension (usually, shrinkage) and the bulk refractive index.

One way to alleviate the shrinkage problem is to separate the photochemical reaction during holographic recording from the polymerization of the host monomer molecules during material preparation. This can be achieved if the material operation can be arranged so that the host polymer matrix is responsible for supporting the binder matrix and the doped molecules are only the photosensitive elements responsible for forming the refractive index holograms.

In making the PQ:PMMA samples, our strategy is to form the host polymer matrix during the material preparation so that only a few percent of unreacted monomer molecules are left for optical exposure usage during holographic recording. It is known that the polymer matrix PMMA can be formed through the thermal chain reaction of MMA monomers by using the thermal initiator azobisisobutyronitrile (AIBN). The key point is to control the environmental parameters for material preparation so that the most of the monomer molecules will be polymerized and only the necessary percentage of unreacted monomer molecules will be left in the material.

After a series of experiments, we have found that a two-step procedure can produce bulk samples of PQ:PMMA with good optical quality. In the first step, \( \approx 0.5 \) wt% of AIBN and up to 0.7 wt% of PQ molecules were dissolved in a solvent MMA and mixed thoroughly to form a uniform solution. The solution was purified, poured into a glass container, and then put in a pressurized chamber. In this stage, the temperature was kept at room temperature for about 120 h until the solution turned homogeneously viscous. During this period, because of the low rate of thermopolymerization at low temperature, the nitrogen molecules released from the thermodecomposition of AIBN and the heat produced from the chain propagation of the MMA monomers could leave the liquid completely. This technique could avoid formation of residual air bubbles and thus reduce the scattering centers in the sample. In the second step, the temperature of the chamber was elevated to 45 °C and held for 24 h to accelerate the thermodecomposition of AIBN. The chain reaction was accelerated and the polymerization was completed. The sample then became a solid block with good optical quality.

In order to measure the ratio of the residual MMA molecules in our PQ:PMMA polymers we performed thermal gravimetric analysis using a DuPont thermal gravimetric analyzer. The result is shown in Fig. 1. It is seen that our sample shows a thermally induced weight change in two stages. In the first stage, which occurs at temperatures below 304 °C, the weight loss is about 10%. In the second stage, which occurs at temperatures above 304 °C, the weight loss is about 90%. Since an MMA molecule is much smaller than a PMMA molecule, the decomposition temperature of the MMA is lower than that of the PMMA. Hence, we can attribute the weight decrease in the low-temperature regime to the thermally induced loss of MMA molecules, and the weight decrease in the high-temperature regime to the loss of PMMA polymer. This implies that in our PQ:PMMA samples about 90% of MMA molecules are polymerized to form PMMA (before thermopolymerization) and about 10% of MMA molecules remain as residual monomers. These residual monomers, together with the PQ molecules, can be used for holographic recording.

During the holographic recording, the photosensitive PQ molecules absorb photons and become radicals, so that they can bond with those \( \approx 10\% \) residual monomer molecules. Preliminary studies on the mechanism of holographic recording in PQ:PMMA showed that the bonding of PQ to MMA could be made one to one. This bonding of the molecules can induce a strong change in the refractive index. Consequently, a large difference in the refractive index between the dark region and the bright region is created. During this exposure procedure, the photosensitizers and residual monomers that are involved in forming the hologram are only a small fraction of the material composition. Thus, the host polymer matrix structure can be maintained unaffected during the optical recording. As a result, the dimensional shrinkage and the bulk refractive index change induced by the recording process can be minimized.

3 Optical Characteristics of the Samples

Our PQ:PMMA samples are yellowish, with clear optical transmission. We have measured the optical transmission spectrum of the samples at different thicknesses. The samples possess strong absorption below blue wavelength (<450 nm), and they are totally transparent for wavelengths longer than 540 nm. In the following experiments we used an argon laser with wavelength 514.5 nm. At this wavelength, the absorption of a 1.2-mm-thick sample is \( \approx 30.2\% \), and that of a 2.4-mm-thick sample is \( \approx 44\% \). The corresponding absorption coefficient is \( \approx 2.7 \text{ cm}^{-1} \).

To test the optical quality of our sample, we used a USAF resolution test chart as the input image to illuminate a 4.8-mm-thick sample. The sample is placed near the Fourier plane of the imaging lens. Figure 2 shows a photograph of a directly transmitted image. It can be seen that the image retains a clear fidelity, which is down to number 6 of group 5. Thus, the resolution capability is estimated to be at \( \approx 95 \text{ lp/mm} \), which is close to the resolution limit of our CCD. The distortion of the image and the scattered noise...
seem to be very small. For volume holographic storage, thousands of pages will be superimposed at a single location of a thick recording material. As the number of recorded pages becomes large, the diffraction efficiency of each hologram will become very weak (~ typically less than $10^{-6}$), and particular attention must be paid to keeping material scattering noise to a minimum. Thus, it is very important to grow a material with very few scattering centers and with high homogeneity in the refractive index. Our two-step technique for material preparation seems to produce samples with satisfactorily uniform refractive index suitable for high-density holographic storage.

4 Characteristics for Holographic Data Storage

4.1 Holographic Recording of the Sample

We first wrote a hologram in a PQ:PMMA sample 4.8 mm thick. Two beams of collimated light from an argon laser were symmetrically incident into the sample with an intersection angle of 32 deg outside the sample. This recording angle is not optimized for our samples. After a series of experiments at different recording angles, we found that the samples have reasonably wide spatial-frequency response. The details for spatial-frequency response measurement are given in the following section. During the single-grating recording, the diffraction efficiency is measured in real time by use of a weak 632.8-nm He-Ne-laser beam at the Bragg-matched angle. The measured curve is shown in Fig. 3. It is seen that the diffraction efficiency (the diffracted light intensity divided by the transmitted light intensity plus the diffused light intensity of the reading beam after the sample) reaches a maximum of 60% at the exposure energy of 0.3 J/cm$^2$, and then it begins to drop on further exposure. At that moment, we also observed distortions in the geometrical shape of the transmitted beam. The beam distortion and the drop of diffraction efficiency are considered to be caused by noise gratings. The noise gratings were initially formed by the scattered beams, which were produced by scattering centers such as microscopic air bubbles and/or the nonuniformity of the refractive index of the photopolymer. Because of the long interaction length in the bulk volume, the scattered beams interfered and the noise gratings were formed and accumulated. This effect could further enhance the nonuniformity of the refractive index of the photopolymer. Thus, the scattering became worse. When the noise gratings became strong, most energy of the incident light was scattered and the diffracted beam became weakened and distorted. The implication of this cumulative effect of the scattered noise is that there should be an upper limit to the exposure time for each holographic recording; otherwise the noise grating will deteriorate the reconstructed image.

In order to determine the upper limit for a single exposure time, we have performed an experiment to quantify the scattering effect. A collimated laser beam with 4 mW/cm$^2$ and 6-mm diameter was incident on a 2.4-mm-thick PQ:PMMA block. We measured the transmitted power within the incident beam as a function of time. As the exposure continues, the scattered noise arises and the directly transmitted power becomes weaker and weaker. If we plot the scattering ratio, defined as the total power scattered outside the beam geometry divided by the initially transmitted beam power, against the exposure, then the dynamics of the scattering can be observed, as shown in Fig. 4. It can be seen that the scattering ratio rose to 70% when the exposure energy reached 2.08 J/cm$^2$. This curve implies that, in order to avoid the buildup of the strong scattering of the recording beams, an upper limit for a single exposure time is necessary. In practice, the optimal exposure time can be determined by taking account of the dynamics of the scattering ratio and also the acceptable signal-to-noise ratio of the photodetector device.

4.2 Diffraction Efficiency of the PQ:PMMA Samples

The dynamic range of a holographic material is a criterion for describing its capability for multiple recording. For a given number of exposures, larger dynamic range of the material will give higher diffraction efficiency of each hologram. Put another way, if the sensitivity of the photode-
In order to find the $M_\#$ of our samples, we performed a hologram recording using the technique of peristrophical multiplexing. Three hundred fifty plane-wave holograms, each with the same exposure energy ($\approx 8 \text{ mJ/cm}^2$), were recorded at a single location of the polymer samples. The diffraction efficiency of each hologram was measured, and then the square roots of the diffraction efficiencies were summed to obtain a running curve of the cumulative grating strength (defined as $C = \sum_{i=1}^{N} \sqrt{\eta_i}$, where $N$ is the total number of exposed holograms) as a function of the cumulative exposure energy. Since $M_\#$ is a systematic parameter, it depends not only on the material but also on the recording geometry.

First, we measure the running curves for polymer samples with different thickness. The results are given in Fig. 5. These curves indicate the recording dynamics of our PQ:PMMA samples. According to Eq. (2), saturation value of the cumulative grating strength is equal to $M_\#$. Thus, the $M_\#$ of our photopolymer sample with different sample thickness can be estimated by using Fig. 5, as shown in Fig. 6. It can be seen that in Fig. 6, $M_\#$ increases linearly with the thickness of the polymer samples, and for the 7.2-mm-thick samples it can be as large as 14. According to the diffraction formula for a volume phase grating, the refractive index change of the photopolymer can be estimated to be $3.1 \times 10^{-4}$.

In addition, we investigated the dependence of $M_\#$ on recording angle. The results for 1-mm-thick samples are shown in Fig. 7. It can be seen that $M_\#$ remains constant as the recording angle changes from 10 to 50 deg. These results demonstrate that our PQ:PMMA samples have reasonably wide spatial-frequency response for the transmission-type holograms. In fact, the material also works well for larger recording angles, such as the 90-deg geometry to be described in Sec. 5.

### 4.3 The Exposure Schedule for Multiple Holographic Storage

Figure 8 shows the diffraction efficiencies of 355 holograms, which were peristrophically (1-deg rotation between holograms) multiplex-recorded in a 4.8-mm-thick sample. Each hologram was recorded with the same exposure energy of 8 mJ/cm². It can be seen that there is a big difference in diffraction efficiencies between the initial and final holograms. For the beginning exposures, the diffraction efficiency of each hologram remains almost constant, and then it decreases as the exposure number is increased. This phenomenon is understandable in that as the exposure is increased the PQ molecules of the photopolymer material start to be exhausted and thus the holograms become weaker and weaker. This behavior is manifested by the...
saturation of the cumulative grating strength shown in Fig. 5. Thus in order to obtain equal diffraction efficiency for the multiple hologram recording, a recording schedule is necessary. The schedule can be obtained from the dynamic behavior of the recording. In order to find a mathematical expression for the dynamic behavior of the recording, we have performed a curve fitting for Fig. 5. The cumulative curves are represented by the solid lines in Fig. 5, given by the exponential function shown below:

\[ C = C_{\text{sat}} \left[ 1 - \exp \left( -E/E_\tau \right) \right], \tag{3} \]

where \( C_{\text{sat}} \) represents the saturation value of the cumulative grating strength, \( E \) represents the cumulative exposure energy, and \( E_\tau \) represents the characteristic exposure energy for each sample, which can be obtained by the curve-fitting procedure of Fig. 5. Based on this formula, we now propose two methods for achieving equal grating strength: the scheduled exposure method and the incremental exposure method.

### 4.3.1 Scheduled exposure method (SEM)

The idea of this exposure method is that by assigning the same grating strength to each exposure, uniform diffraction efficiencies can be achieved. The grating strength of each hologram can be found by dividing the saturation grating strength into \( N \) equal intervals \( C_{\text{sat}}/N \). The recordation times for each hologram can be determined before recording. This method can be performed graphically by use of Fig. 5. Firstly, the grating strength of each hologram, \( C_{\text{sat}}/N \), is marked along the vertical axis. Secondly, the exposure energy for each exposure can be assigned by mapping the grating strength of the vertical axis to the corresponding point on the horizontal axis. This procedure can also be performed with an analytical method. Assuming that each exposure energy is very small (compared with the total energy required for the saturation exposure), then by differentiating Eq. (3), the growth rate of the cumulative grating strength as a function of the exposure energy can be obtained as

\[ \Delta C = \frac{\partial C}{\partial E} \Delta E = \frac{C_{\text{sat}}}{E_\tau} \exp \left( \frac{E}{E_\tau} \right), \tag{4} \]

where \( \Delta C \) is the grating strength increment corresponding to the exposure energy \( \Delta E \). Furthermore, \( \Delta E \) can be defined as \( I \Delta t \), where \( I \) is the input light intensity and \( \Delta t \) is the exposure time for the \( n \)th hologram. Denoting \( \Delta t \) by \( t_n \), then the exposure schedule can be written as

\[ t_n = \frac{1}{I} \int \frac{\Delta C}{E_\tau} \left[ \exp \left( \frac{1}{E_\tau} \sum_{i=1}^{n-1} E_i \right) - 1 \right] \]

For equal strength of each hologram, \( \Delta C \) can be obtained as \( C_{\text{sat}}/N \). The exposure time for each hologram can be determined before recording as long as the material characteristics \( E_\tau \) and system parameters \( I, N \) are given. This method is therefore called as scheduled exposure method (SEM).

As a demonstration for the SEM, a 4.8-mm-thick sample was used to record 350 holograms. The parameters are \( E_\tau = 0.6 \text{ J/cm}^2 \), \( N = 350 \), and \( I = 4 \text{ mW/cm}^2 \). The exposure time for each hologram was calculated and is shown in Fig. 9. It is seen that the exposure time is no longer a constant and it increases greatly for the final hologram. The diffraction efficiencies of the first 300 holograms that were recorded with this exposure schedule were measured and are shown in Fig. 10. Comparing them with those shown in Fig. 8, we see that the diffraction efficiencies are much more uniform.

### 4.3.2 Incremental exposure method (IEM)

Another method to obtain equal strength of the gratings is to record all holograms successively and repeatedly, using identical exposure energy for each exposure. Each time the exposure energy is much smaller than the characteristic exposure energy \( E_\tau \). The idea of this recording method is

\[ \Delta C = \frac{\partial C}{\partial E} \Delta E = \frac{C_{\text{sat}}}{E_\tau} \exp \left( \frac{E}{E_\tau} \right), \tag{4} \]

where \( \Delta C \) is the grating strength increment corresponding to the exposure energy \( \Delta E \). Furthermore, \( \Delta E \) can be de-

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**Fig. 8** The diffraction efficiency of 355 holograms each with equal exposure energy.

**Fig. 9** The exposure time for each hologram by use of the SEM schedule.

**Fig. 10** The diffraction efficiencies of the 300 holograms recorded with the SEM exposure schedule.
schematically shown in Fig. 11. In the first cycle, all the holograms are successively recorded in the polymer with an identical exposure energy, with a recording sequence from 1 to \( N \) (\( N \) is the number of holograms). In the second cycle, again all the holograms are exposed with the same exposure energy, but this time they are recorded with the reversed recording sequence (i.e., from \( N \) to 1). The purpose of the second sequence is to provide a compensation for the saturation of the photopolymer in the first cycle. For the third cycle, the exposure sequence is reversed again (i.e., from 1 to \( N \)), and so on for the further exposure cycles.

This recording procedure is repeated until a steady state of the grating strength is reached. By using the recording dynamics [Eq. (3)] and a recursive derivation, the cumulative grating strength of the \( j \)th hologram at the end of the \( q \)th recording cycle can be obtained as follows:

\[
C_j = 
\frac{C_{sat} \Delta E}{E_\tau}
\left[
\exp\left(-\frac{\Delta E}{E_\tau (j-1)}\right) + \exp\left(-\frac{\Delta E}{E_\tau (2N-j)}\right)
\right]
\times
\left[
1 + \exp\left(-\frac{\Delta E}{E_\tau 2N}\right) + \exp\left(-\frac{\Delta E}{E_\tau 4N}\right) + \cdots
\right]
\frac{1}{1 - \exp\left(-\frac{\Delta E}{E_\tau 2N}\right)}
\]

\[
\approx 
\frac{C_{sat} \Delta E}{E_\tau}
\left[2 - \frac{\Delta E}{E_\tau (2N-1)}\right]
\left[
\frac{1 - \exp\left(-\frac{\Delta E}{E_\tau 2N}\right)}{1 - \exp\left(-\frac{\Delta E}{E_\tau 2N}\right)}
\right]
\]

if \( (2N-1) \Delta E \ll E_\tau \), \hspace{1cm} (6)

where \( N \) is the total number of holograms, \( \Delta E \) is the exposure energy for each exposure, and \( q \) is the number of recording cycles. It can be seen in Eq. (6) that the cumulative grating strength for each hologram is a constant, independent of the hologram number \( j \). Note that this method is similar to the incremental recording method for photorefractive materials, proposed in Ref. 16. Therefore, this technique can be called the incremental exposure method (IEM).

The SEM and IEM each have their pros and cons. In the SEM the holograms are recorded one after another by using the predetermined recording schedule. The recording procedure is completed in one cycle. Because of the saturation of the photopolymer, the exposure time for a new hologram should be longer than that of the preceding one. The recording time for the last holograms can be very long. For the last holograms the polymer is getting close to material saturation, and the noise gratings are easily formed, so that the quality of the stored image can be degraded. However, since all holograms are recorded in one cycle, this method has the advantage of easy addressing of the reference beams. In contrast, the holograms with the IEM method are recorded in many cycles. Hence, to assure the accumulation of the strength of each grating, accurate addressing of the reference beams during all the recording cycles is necessary. It requires a precise and stable mechanism for the reference beams to achieve this task. In addition, because of the requirement of many repeated recording cycles, it may take a long time to display the image on the input spatial light modulator, so that the recording procedure is slow. Nevertheless, because the energy for each exposure is much smaller than the characteristic exposure energy, the noise gratings may be much weaker and the image quality may be better than that of the SEM recording procedure.

## 5 Multiple-Image Storage Experiment

We have performed a multiple-hologram storage experiment using a PQ:PMMA bulk photopolymer. A 1\( \times \)1 \( \times \)1-cm\(^3\) photopolymer cube with 0.6% PQ was used in the experiment. The experimental setup is a typical angle-multiplexing system with 90-deg geometry. The reference and signal beams were incident into the photopolymer sample through adjacent sides of the cube. The intensity of each beam was 2 mW/cm\(^2\). Two hundred and fifty Fresnel holograms of a chessboard pattern, which was shown on a liquid-crystal television (LCTV) with resolution of 320 \( \times \) 240 pixels, were recorded in a single location. Each step of the angle separation was about 0.02 deg.

The exposure time for each hologram was conducted by the SEM recording schedule with a characteristic exposure energy constant of 1.6 J/cm\(^2\) for the photopolymer sample. The original and 11 reconstructed images are shown in Fig. 12. It is seen that the reconstructed images have as good fidelity as the original image. Because the complete images can be reconstructed from such a 1-cm-thick block, we conclude that shrinkage is negligible in our sample. This experimental result demonstrates that, so far as the shrinkage problem is concerned, our photopolymer samples are suitable for volume holographic storage.
6 Conclusions

We have presented a method for synthesizing thick bulk high-optical-quality photopolymer material for volume holographic data storage. Optical properties of the photopolymer have been measured, and the limit of a single exposure time for avoiding the building up of scattering noise has been described. By measuring the recording dynamics of multiple holograms in these photopolymer samples, the characteristics of this new recording material have been investigated. Based on these studies, the criterion for evaluating the dynamic range for holographic recording, expressed as the $M_\#$ of the polymer, has been described. The $M_\#$ can be as large as 14 for 7-mm-thick samples. The samples have reasonably wide spatial-frequency response. Using the recording dynamics of our polymer samples, two recording schedules for achieving uniform diffraction efficiencies for multiple storage have been proposed. These two methods are also applicable for any material with saturation recording dynamics. The volume holographic storage of 250 Fresnel holograms in a $1 \times 1 \times 1$-cm$^3$ cube sample has been experimentally demonstrated. The experimental results show that the shrinkage effect in this thick material is negligibly small, so that the material is very attractive for volume holographic data storage.

Acknowledgments

This research is supported in part by the Ministry of Education under contract 89-E-FA06-1-4, and in part by the National Science Council, Taiwan, under contract NSC90-2112-M-009-032.

References