

Phenanthrenequinone-doped poly(methyl methacrylate) photopolymer bulk for volume holographic data storage

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We present the design and fabrication of a phenanthrenequinone-doped poly(methyl methacrylate) photopolymer material. Large blocks of samples were made, and the material showed negligible shrinkage after optical exposures. We recorded and reconstructed 250 holograms at a single spot, using a 1-cm³ block. © 2000 Optical Society of America

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Holographic data-storage systems with high storage capacity, high data-readout rate, high image quality, and low bit-error rate have been proposed and demonstrated.¹⁻³ By use of a suitable multiplexing scheme based on Bragg diffraction, thousands of pages of optical information have been superimposed and recorded at one location in a recording medium. In these systems thick recording material with high optical quality is the key component. However, when the thickness of the recording material is increased, particular attention must be given to achieving low optical scattering and avoiding material shrinkage during optical exposure, which both degrade the fidelity of the readout page. The thicker the photopolymer recording medium, the more serious the dimensional shrinkage. Compared with photorefractive crystals, polymer-based material is easy to fabricate, but scattering noise and shrinkage problems are much more serious with polymer holograms.⁴ Therefore polymer researchers have focused their efforts on synthesizing new, thick materials.⁵⁻⁷ Phenanthrenequinone- (PQ-) doped poly(methyl methacrylate) (PMMA) photopolymer was fabricated and characterized in the studies reported in Refs. 6 and 7. We were attracted by the no-shrinkage property of this material, as mentioned in Ref. 7. In this Letter we present our studies of the design and fabrication of PQ-doped PMMA photopolymer bulk materials. Based on our material preparation technique, high-optical-quality samples with large dimensions of as much as 2.5 cm × 2.5 cm × 2.5 cm have been made, and new results have been observed in our samples. We report the multiple storage and reconstruction of 250 holograms at a single spot by use of a 1-cm³ photopolymer block.

We first briefly describe our design strategy for making bulk samples with minimal dimensional shrinkage. Most photopolymer materials consist of a photopolymerizable monomer, a photoinitiator, and a sensitizer in a polymer binder. During optical exposure, a few photons can initiate a chain reaction of photopolymerizable monomer molecules, which causes

a change of the refractive index, forming a hologram. Because a large number of monomer molecules are involved in the formation of the hologram, the material exhibits significant dimensional shrinkage. One possible way to alleviate this problem is to separate the photochemical reaction from the polymerization of the monomer molecules. Our photopolymer samples consist of two components: PMMA, which is the host polymer that supports the polymer matrix, and PQ, the doped molecules that are the photosensitive elements that form the refractive-index holograms. During material preparation, most of the monomer molecules are polymerized to form the host polymer matrix. Only a small percentage of monomer molecules that have not reacted is left, and these molecules, together with photosensitizers, are uniformly distributed in the host polymer matrix. This process can be called prepolymerization. Using a thermal gravimetric analyzer, we showed in our chemical analysis that ~10% of the methyl methacrylate (MMA) in our samples was the residual monomers. During optical exposure, under illumination the photosensitized PQ molecules absorb photons and become radicals, bonding with the residual monomer molecules on a one-to-one basis. The primary chemical reaction occurs in the bright region. Free PQ and MMA molecules diffuse from the dark into the bright regions. Consequently, a difference between the refractive indices in the dark and the bright regions is created; i.e., a phase grating is formed. This reaction induces a large refractive-index change and forms a strong phase hologram. Because the residual monomers and photosensitizers involved in the formation of the hologram are only a small fraction of the compositions, the host polymer matrix structure can be maintained during optical recording. As a result the dimensional shrinkage and the bulk refractive-index change induced by the recording light are minimized. In addition, at room temperature the monomer molecules MMA are small enough to diffuse through the host PMMA polymer matrix. The bonded PQ:MMA molecules are much larger, such that they

experience only minimal diffusion. Heat treatment after optical exposure is not necessary for the recorded hologram to be revealed, and the hologram can be fixed automatically if all the PQ (0.6%) molecules are exhausted.

We performed an experiment involving illumination of a yellow liquid mixture of MMA monomers and PQ molecules that provides evidence for our proposed model. We observed that exposure to light caused the liquid to become colorless. This behavior is similar to that of the polymer sample. However, exposure to light did not turn the liquid into a solid. In addition, we analyzed the chemical component of the exposed liquid with a gas chromatograph–mass spectrometer. The result is shown in Fig. 1. It can be seen that the peaks corresponding to the single pair of PQ:MMA and the fragments of PQ:MMA molecules (which were produced during measurement with the gas chromatograph–mass spectrometer) are much stronger than those of larger molecules. These results imply that illumination did not cause photoinduced polymerization of the MMA molecules. Therefore we believe that in our materials bonding of PQ molecules with residual MMA monomers is the main photoinduced reaction.

We now present our material preparation technique for making bulk material with larger dimensions. Our PMMA host matrix was made from the chain reaction of polymerization of MMA monomers by use of a thermal initiator, azobisisobutyronitrile (AIBN). To preserve the uniformity of the refractive index inside the bulk sample we made the polymer blocks in two stages at different temperatures. In the first stage we prepared the samples by dissolving the initiator, AIBN ($\sim 0.5\%$), and the PQ molecules ($\leq 0.7\%$) in the solvent MMA. We purified the solution to remove the undissolved particles and thus reduce the light-scattering centers. The purified solution was poured into a square glass tube and then put in a chamber at room temperature for ~ 120 h until the solution turned homogeneously viscid. During this stage, nitrogen molecules were released from the thermodecomposition of AIBN, and heat was produced from the chain propagation of MMA monomers. Because of the slow polymerization rate at low temperature, both byproducts were completely exhausted from the material. Therefore there were no residual air bubbles left in the sample, and the uniformity of the material could be maintained. In the second stage the temperature of the chamber was increased to 45°C for 24 h. The thermodecomposition rate of AIBN as well as the chain reaction was accelerated until polymerization was complete. The sample then became a solid block, and high-optical-quality polymer cubes were thus obtained. The dimensions of the blocks were determined by the geometry of the glass tube, which could be approximately $1\text{ cm} \times 1\text{ cm}$ to $2.5\text{ cm} \times 2.5\text{ cm}$, with a thickness of 1–25 mm. Figure 2 shows a photograph of the image of a U.S. Air Force resolution test chart directly transmitted through a 4.8-mm-thick PQ:PMMA block. It can be seen that the image retains clear fidelity, down to the number 6 of group 5. In our system the resolution seems to be ~ 95 line pairs/mm, which is close to the limitation of our CCD. In this

respect our technique of prepolymerization can produce satisfactory index uniformity inside the sample for high-density holographic storage. In the following experiments we used polymer samples doped with 0.6% PQ and 0.5% AIBN molecules. Our PQ:PMMA blocks appear to be yellow. We measured the optical transmission of different samples in the visible range. The samples have an absorption coefficient of $\sim 2.7\text{ cm}^{-1}$ for the wavelength of 514.5 nm that we used in the experiments.

To examine the dimensional shrinkage effect in our polymer samples we performed a multiple-hologram storage experiment on a polymer cube, using a 90° -geometry recording setup. This particular setup provides the most critical Bragg selectivity, such that the shrinkage effect can be well examined and the storage capacity can be maximized.¹ A $1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ polymer cube was used. A schematic diagram of the optical setup is shown in Fig. 3. The reference and the signal beams were incident upon the cube at adjoining sides. The intensity of each beam was 2 mW/cm^2 . Angle multiplexing was achieved by rotation of mirror M1 in a telescope structure of the reference arm. We recorded 250 Fresnel holograms in a chessboard pattern, which was shown on a liquid-crystal television with a resolution of 320×240 pixels in a single location. The sample was located near the Fourier plane

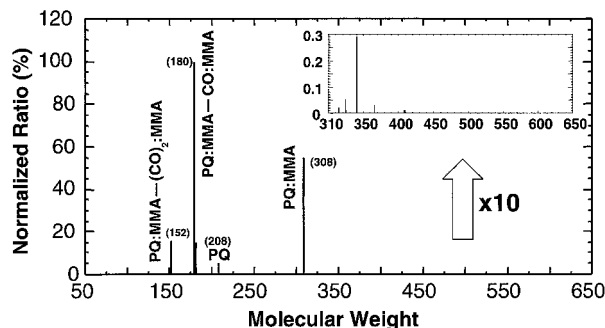


Fig. 1. Molecular weight analysis spectra of the liquid sample of the exposed PQ and MMA mixture. The labels PQ:MMA-CO:MMA and PQ:MMA-(CO)₂:MMA indicate that the CO:MMA components have been removed from the PQ:MMA molecule by a gas chromatograph–mass spectrometer.

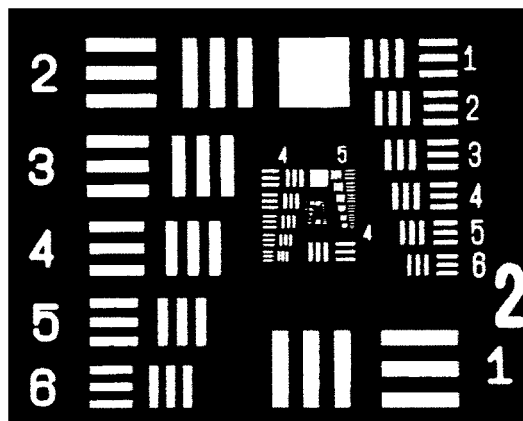


Fig. 2. Photograph of an image directly transmitted through a 4.8-mm-thick block.

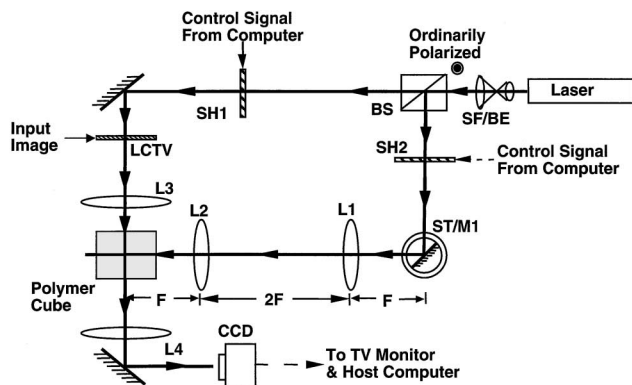


Fig. 3. Schematic diagram of a 90°-geometry recording setup: BS, beam splitter; SH1, SH2, shutters; L1–L4, lenses; F, focal length; LCTV, liquid-crystal television; SF/BE, spatial filter–beam expander. ST/M1, mirror 1.

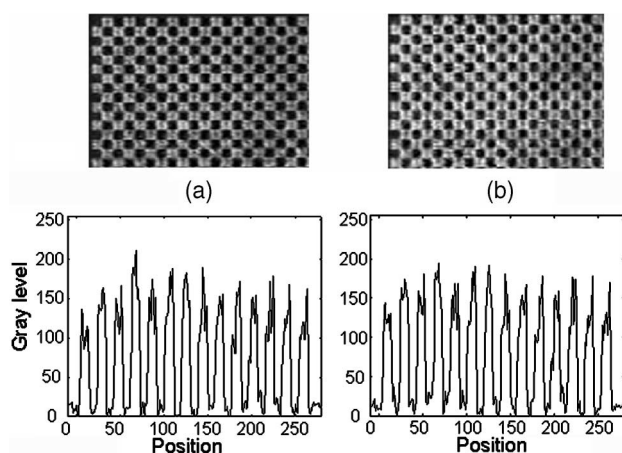


Fig. 4. Photographs of (a) the original and (b) one of the reconstructed images, and the corresponding gray-scale distribution along an arbitrary horizontal line on each image.

of lens L3. Each step of angle separation was $\sim 0.02^\circ$, which was the resolution limit of our rotation stage.

The exposure time of each hologram was controlled by a suitable schedule, which was designed to compensate for the saturation effect in a typical photopolymer material so that the retrieved holograms maintained almost equal diffraction efficiency. Obviously each subsequently recorded hologram should require a longer exposure time than the previous one. The detailed design rule was presented in Refs. 8 and 9. The average exposure energy of our sample was $\sim 5 \text{ mJ/cm}^2$. The resulting diffraction efficiency of each hologram was $\sim 1.5 \times 10^{-4}$. The original transmitted image and one of the reconstructed images are shown at the top of Fig. 4. The graphs at the bottom of the figure show the gray-scale distribution along an arbitrary horizontal line on each image. It can be seen that the reconstructed image has almost the same fidelity as the original transmitted image. The whole page of the image can be also reconstructed completely from such a 1-cm-thick block

at every angle that it was recorded. This implies that the shrinkage effect is almost negligible in our samples.

The $M/\#$ was used as a metric for characterizing the storage capability of a holographic storage material.¹⁰ To measure the $M/\#$ we performed a peristrophically multiplexed holographic storage experiment. We recorded 355 plane-wave holograms, each with equal exposure energy ($\sim 8 \text{ mJ/cm}^2$) and at a writing angle of 32° outside the material. The diffraction efficiency of each hologram was measured, and we summed the square roots of the measured diffraction efficiencies to obtain the $M/\#$ value. The results show that the $M/\#$ increases linearly with the thickness of the polymer sample. For a 8-mm-thick polymer $M/\#$ is as large as 14. Based on this value, if we can achieve a diffraction efficiency for each hologram of 4×10^{-6} ,² then the total number of pages that can be recorded at a single spot can be estimated to be 7000. This result suggests that our PQ:PMMA polymer can be used for large-capacity holographic data storage.

In summary, we have made a new PQ:PMMA photopolymer. A novel physical mechanism has been proposed to explain the optical exposure process in our samples. The shrinkage effect in this very thick material is negligibly small, so the material is very attractive for holographic data storage. Our PQ:PMMA polymer sample had $M/14$ for an 8-mm-thick sample. This $M/\#$ is close to the expected value reported in Ref. 7, which is $M/4.8$ for a 3-mm-thick sample. The main advantage of our sample is that baking is not required for the recorded hologram to be revealed. It is also useful for practical applications.

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