

Analyses on physical mechanism of holographic recording in phenanthrenequinone-doped poly(methyl methacrylate) hybrid materials

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Abstract. The photoproducts in phenanthrenequinone (PQ)-dissolved methyl methacrylate (MMA) liquid samples and PQ-doped poly(methyl methacrylate) (PQ/PMMA) solid photopolymer samples have been analyzed by various chemical measurements. A mechanism for holographic recording in our PQ/PMMA photopolymer is proposed. By UV-VIS transmission and photoluminescence spectral measurements, we find that under light exposure the molecular structure of PQ is transformed to be less conjugated. The measured results of mass spectra, Fourier transform infrared spectra, NMR spectra, and gel permeation chromatograph analyses provide some evidence for recognizing the molecular structure of the photoproducts in our PQ/PMMA photopolymers. The results show that under light exposure the PQ and MMA form new molecules, mainly an adduct of one PQ molecule with one MMA molecule. In addition, PQ also reacts as a photoinitiator to form PMMA oligomers in our samples. The structure change of the PQ molecule induces a strong change of the refractive index in the material. It provides a mechanism to record a phase hologram in our PQ/PMMA photopolymer. Holographic recordings in the samples are demonstrated, and the dynamic range of the sample is investigated. © 2004 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.1774196]

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1 Introduction

Holographic data storage has been considered one of the promising information storage technologies because of its distinct advantages of large storage capacity and fast data access rate. In recent years many research efforts have been invested on this topic and rapid progress has been achieved. Several holographic data storage systems with very large storage capacities, high data readout rates, and low bit error rates have been demonstrated.^{1,2} However, before this technology can be successful for practical applications there are several fundamental issues necessary to be resolved. One of the fundamental issues is the lack of suitable recording material.

To be good holographic data storage material, many characteristics are required, such as high optical sensitivity, simple development procedures, uniform spatial frequency response, large diffraction efficiency, high optical quality, and long-term stability. For volume holographic storage using thick materials, good optical quality and dimensional stability are the most crucial requirements. Among the current recording materials, photopolymer materials are the most popular and suitable for the holographic write-once-read-only-memory (WORM) system. Many experimental works have been demonstrated about the feasibility of using polymer-based materials for holographic data storage.³⁻¹⁰ These materials can provide large modulation in refractive index, and they are easy to fabricate because

dedicated crystal growing facilities are not required. On the other hand, they also have some disadvantages. Among them, the material shrinkage effect induced by holographic recording is the most serious. This effect will induce dimensional distortions on the recorded gratings so that the Bragg condition for volume holograms is lost and the recorded information cannot be retrieved completely.¹¹ The shrinkage effect is to some extent proportional to the material thickness. As a result, a typical thickness of conventional photopolymer material is limited to a few hundred microns.

By using a prepolymerization technique, we have succeeded in making phenanthrenequinone (PQ) dye-doped poly(methyl methacrylate) (PMMA) photopolymers, which have a very attractive optical quality and negligible photo-induced shrinkage.^{12,13} Our idea for alleviating the shrinkage problem was to separate the photochemical reaction during holographic recording from the polymerization of the host monomer molecules during material preparation. Based on this idea, we investigated the technique to synthesize a photopolymer material, so that a polymer matrix is used for supporting the binder matrix and only the doped molecules are used as the photosensitive elements to form the refractive index holograms. The key is how to ensure the photoreaction of the doped PQ molecules during holographic recording without affecting the backbone structure of the PMMA matrix. In fact, during holographic exposure it requires corresponding components to take part in photo-

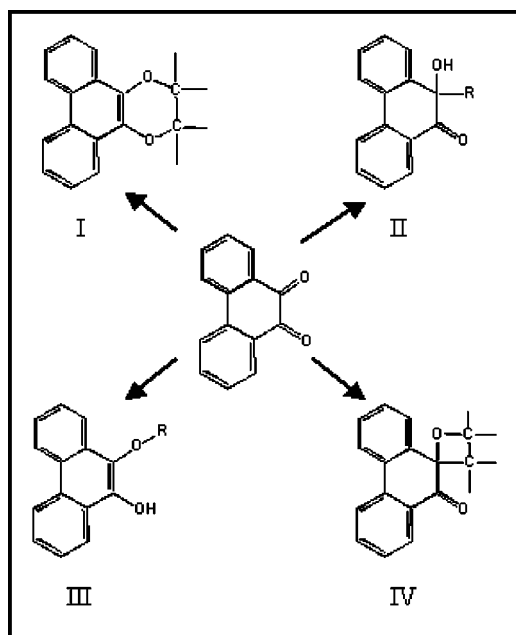


Fig. 1 The four different ways to combine a phenanthrenequinone molecule with an olefin-based molecule.

reaction with PQ molecules. A possible component for this function would be MMA monomers. Therefore, our technique is to control the environmental parameters for material preparation such that most of the monomer molecules are polymerized, and only the necessary percentage of unreacted monomer molecules are left for later photoreaction during the holographic recording stage. After a series of experiments, we have found a two-step procedure that can synthesize bulk samples with satisfactory optical quality.¹² Investigations show that environmental parameters have a strong influence on photopolymer characteristics. A comparison of the recording mechanisms has been made between the different photopolymers grown by diverse fabricated ways from the viewpoint of optical recording behaviors.¹⁴ In addition, characteristics of photo- and thermo-reactions of PQ molecules with olefin-based molecules have been studied.¹⁵ The results show that during light exposure of the photopolymer material the *o*-quinones on the PQ molecules may bond to the olefins on the MMA molecules. Under photo- and/or thermo-reactions, four different routes might be taken in the form of one PQ molecule to one MMA molecule bonding structure, as shown in Fig. 1. These four routes all lead the PQ molecules to become less conjugated, so that the refractive index of the photopolymer can be changed via photo-induced chemical reaction. However, these four photoproducts have different chemical properties such that the stability and change of the refractive index change of the photopolymer samples after light exposure are different. We need more evidence to understand photochemical behavior in our PQ-doped PMMA photopolymers. This information can also provide the details about the holographic recording mechanism.

We report investigations on chemical analyses of our PQ/PMMA samples under light exposure and unexposure conditions. We first briefly review the photopolymer sample preparation method. We then present chemical

analyses for unexposed and exposed samples, both in PQ-doped PMMA solids and PQ-dissolved MMA liquids. These results give us direct observations about the photochemical process, including the behaviors of the *o*-quinones on PQ molecules and the olefins on MMA molecules. Based on these analyses, an optical recording mechanism in our PQ/PMMA sample is then proposed. The holographic recording characteristics are also studied and discussed.

2 Experimental Description

2.1 Material Preparation

The chemical dye molecule 9,10-phenanthrenequinone (PQ), was purchased from Aldrich Chemical Company.¹⁶ The thermo-initiator, 2,2-azo-bis-isobutyronitrile (AIBN), was bought from Showa.¹⁷ The monomer, methyl methacrylate (MMA), was bought from Lancaster Company.¹⁸ To remove the stabilizer from the monomer, the mixture solution of MMA and stabilizer was separated by a vaporizing approach, by which we heated and stirred the monomer to form a gas phase under low pressure. The vapor flew through a cooling tube to form a purified MMA liquid.

2.1.1 Photopolymer fabrication

The PQ molecules were dissolved into the MMA solvent with the weight ratio of 0.7 wt%, which is the saturation concentration. The AIBN molecules of 1 wt% by weight were added. It plays the role of thermal initiator to turn MMA monomers into PMMA polymers. The compound solution was stirred about 24 h under constant temperature at 30°C until the solute was dispersed and mixed well. We then used a filter with a hole size of 0.2 μm to further filter out impurities from the solution. The filtered solution was used to make samples in two stages. In the first stage, it was stirred at 30°C for around 60 h until the solution turned highly viscous. In the second stage, the solution was then poured into a glass cell and baked at 40°C for 3 days. This procedure could induce most of the MMA molecules to be polymerized. This two-step procedure was found to produce bulk samples with good optical quality. Our samples appear to be a yellowish color, with a clear optical transmission. In fact, depending on the temperature for polymerization, the concentration of residual monomer MMA is varied. By use of a thermal gravimetric analysis method, our samples are analyzed to contain around 10% MMA in the photopolymer. After examining the UV-absorption spectrum of the samples, an argon laser with wavelength 514 nm is chosen as the light source for exposure and holographic recording experiments.

2.1.2 Sample preparations

We have performed chemical analyses on the photoproducts of four different samples: the PQ-doped PMMA solid samples (PQ/PMMA), and the PQ-dissolved MMA liquid samples (PQ/MMA), both under light exposed and unexposed conditions. For the exposure, a laser with intensity of 150 mw/cm^2 is used to illuminate samples until the color is changed from yellow to transparent, which means the photosensitizers (PQ molecules) have been exhausted. Comparison of exposed and unexposed samples allow us to identify possible photoreactions in these samples. Furthermore, to investigate if light exposure could induce photo-

polymerization in our samples, we compared chemical analyses on PQ/MMA and PQ/PMMA samples.

During the chemical analyses, the large volume of MMA solvent of the PQ/MMA samples produces a strong background signal. To eliminate this background, the unreacted MMA solvent should be removed from the samples before performing chemical analyses. We have achieved this by putting the samples into a vacuum (~ 0.1 torrs) ovens and baked for 7 days at 40°C .

2.2 Photochemical Measurements

We have performed six chemical measurements to investigate the photoreaction in our samples. They are described as follows: 1. UV-VIS spectra of the exposed and unexposed PQ/PMMA samples were measured by using a Hitachi-U2000. This helps us to know the sensitive wavelengths of our samples as well as the change of conjugation structure of the chemical compounds in the samples. 2. Photoluminescence (PL) spectra measurement of both the PQ/PMMA and PQ/MMA samples were performed by a Hitachi E4500, under exposed and unexposed conditions. This could help us judge the structure change of the chemical compounds under light exposure. In the experiments, the photoproducts of PQ/MMA were resolved with chloroform and poured into a quartz cell. 3. Mass spectra of the PQ/PMMA and PQ/MMA samples were obtained by using a VG Biotech TRIO-2000, under light exposed and unexposed conditions. It provides information about the molecular weight of the compounds and tells us if there is any new compound produced by light exposure. 4. Infrared spectra of the PQ, MMA, and exposed PQ/MMA samples were carried out with a Nicolet Protégé-460 Fourier transform infrared spectrophotometer. It provides information about functional groups of the molecule structure. Before measurement, the exposed PQ/MMA solutions were dipped on KBr plates. The plate samples were baked at 40°C for 7 days such that the unreacted MMA molecules were removed and the pure photoproducts were left on the KBr plates. 5. ^1H - and ^{13}C -NMR spectrum of the exposed PQ/MMA sample was measured by using Varian unity-300. To fit in the instrument, the dried photoproducts from the exposed PQ/MMA liquid were dissolved in dimethyl sulfoxide- d_6 (d-DMSO) solvent and poured into a glass tube. This measurement provides information about the hydrogen-bond compounds and ascertains the molecular structure. 6. The molecular weight distributions of the exposed PQ/MMA, unexposed PQ/PMMA, and exposed PQ/PMMA samples were measured by using a gel permeation chromatographer (GPC) Waters 2414. The GPC analysis is usually utilized to measure the molecular weight of a polymer and identify the degree of purity of the polymer sample. The measurement provides information about whether a photoinduced polymerization occurs in our samples. In the measurements, tetrahydrofuran (THF) was used as the solvent to dissolve the exposed and unexposed PQ/PMMA solid samples.

2.3 Holographic Measurements

For holographic characteristic measurements, an optical setup of typical nondegenerate four-wave mixing has been constructed, as shown in Fig. 2. A collimated light beam from an argon laser with a wavelength of 514 nm was

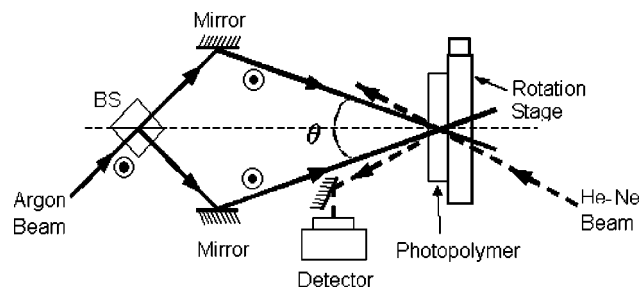


Fig. 2 The optical setup for holographic recording characteristics measurements.

divided into two beams. They are incident onto the sample symmetrically with an intersection angle of 32° outside the sample. The diffraction efficiency of the hologram was measured in real time by use of a weak 632.8-nm He-Ne laser beam at the Bragg-matched angle. The argon laser is a Coherent Innova 300 and the He-Ne laser is a JDS 1144P. In addition, for measurements of the dynamic range, the sample was placed on a rotational stage to perform peristrophical multiplexing for recording multiple holograms.

3 Results and Discussions

3.1 Photochemical Measurements

3.1.1 UV-VIS spectra measurements

In the experiments of UV-VIS spectra, we measured the optical absorption spectrum of the PQ/PMMA with different thicknesses. Typical optical absorption of our samples before and after exposure under a green light (514 nm) is shown in Fig. 3. Before light exposure, the samples possess strong absorption below the blue wavelength (< 450 nm). At 514-nm wavelength, the absorption coefficient is $\sim 2.7\text{ cm}^{-1}$. The samples are totally transparent for wavelengths longer than 540 nm. The results show that our samples are sensitive to the green light of 514 nm and so this wavelength is suitable for holographic recording. After exposure with 514-nm illumination, the absorption band shows a blue shift and the samples have absorption only in

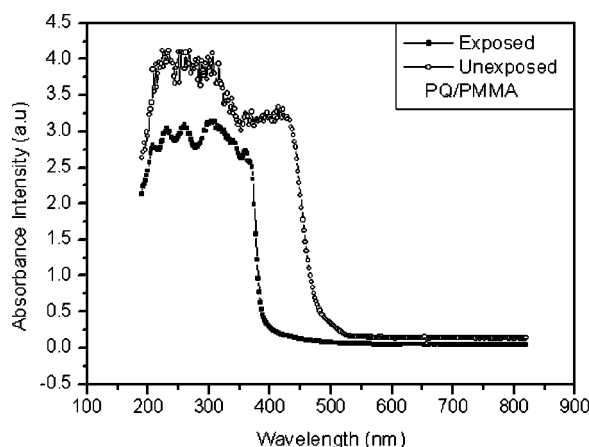


Fig. 3 The UV-VIS absorption spectra of the PQ/PMMA sample with thickness of 1 mm.

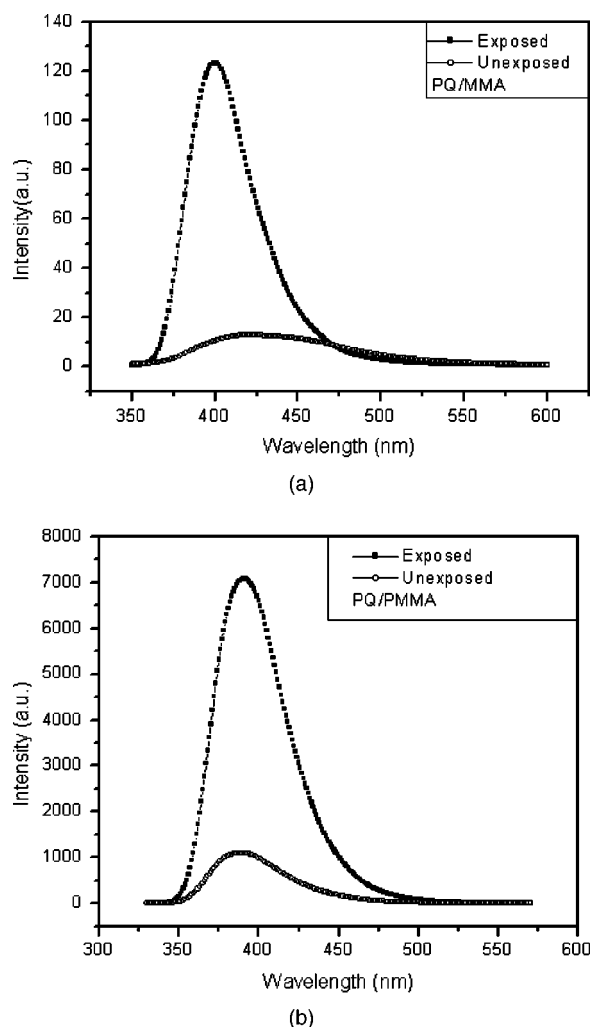


Fig. 4 The photoluminescence spectra of (a) photoproduct extracted from exposed PQ/MMA and unexposed PQ/MMA samples, and (b) unexposed PQ-PMMA and exposed PQ-PMMA solid samples.

the UV regime (<400 nm). This result implies that the structures of the photoproducts become less conjugated than those of the original material.

3.1.2 Photoluminescence spectra measurements

In our measurements, a light source of 300-nm wavelength was used for the excitation. Figure 4(a) shows the PL spectra for PQ/MMA samples. The result shows that the spectrum of the exposed sample has stronger luminescence intensity. It is known that the fluorescence of our PQ/MMA sample mainly results from light-excited PQ molecules. However, for unexposed samples, the well-conjugated PQ molecule has two carbonyl functional groups and is highly coplanar. This molecular structure cause the excited PQ molecules to have strong interaction with other PQ molecules. When the excited PQ molecules transfer from the excited state to the ground state, the released energy is absorbed by the interactions between PQ molecules and transferred into thermal energy. Thus, the excited PQ molecules cannot release energy through radiation such that the intensity of the fluorescence spectrum becomes weak. Under

light exposure, the carbonyl functional group on the PQ molecule has been broken and attached with the vinyl group on the MMA molecule, turning into aromatic ester. In this case, the molecular structure of photo product becomes less conjugated and less coplanar such that the excited aromatic esters have less interaction with other molecules. Therefore, the excited molecules can release energy to the ground state through radiation mechanism, and the intensity of the fluorescence spectrum becomes stronger. This process is usually called the quench effect of the carbonyl groups in PQ molecule. Similarly, the PL spectra for the exposed PQ/PMMA sample also has a stronger fluorescence peak than that of the unexposed PQ/PMMA sample, as shown in Fig. 4(b). We think that the increase of intensity may also be induced by the quench effect of the photoproduct inside the PMMA matrix. This could be an indication that the photoproducts become less conjugated than those of the original PQ molecules.

3.1.3 Mass spectra measurements

From mass spectra measurements, we can see whether there are any new compounds produced by light exposure. Figure 5(a) shows the mass spectra of unexposed and exposed PQ/MMA liquid samples. We find that a new peak signal appears at 308 by molecular weight in the exposed PQ/MMA, which does not appear for the unexposed sample. This means that the peak at 308 is a characteristic difference between the photoexposed and unexposed PQ/MMA, since the molecular weights of PQ and MMA are 208 and 100, respectively. The existence of a peak signal at 308 by molecular weight is evidence that the photoproduct is one MMA molecule attached to one PQ molecule in our PQ/MMA liquid samples. Figure 5(b) shows the mass spectra of PQ/PMMA solid samples. It is also observed that a new peak appears at a molecular weight of 308 for the exposed sample, which is the same characteristic as that shown in Fig. 5(a). In summary, Fig. 5 shows an important characteristic of light exposure for both the PQ/MMA liquid and PQ/PMMA solid samples, i.e., a new compound with a molecular weight of 308 has been formed, which comes from the photoproduct of one PQ molecule attached to one MMA molecule.

3.1.4 FTIR spectra measurements

Figure 6 shows the FTIR spectra of PQ, MMA, and photoproduct extracted from light-exposed PQ/MMA. It can be observed that many absorption peaks occur at different wave numbers, which provide information about the functional groups appearing in different samples. We expect that under light exposure the o-quinone double bond $C=O$ of the carbonyl group on the PQ molecule becomes radical and attaches with the double bond $C=C$ of the vinyl group on the MMA molecule, as shown in Fig. 1. The attachment produces the OH plus the acrylate functional groups in II and III routes, as well as the aromatic ester functional group ($C-O-C$ ring) in I and IV routes. Therefore, in spectra, we check the position of some characteristic peaks, which corresponds to the previous functional groups and then identify the possible routes of the photoreaction.

First, we check the spectral regime larger than wave-number 2000 cm^{-1} . For the PQ, the weak absorption peak

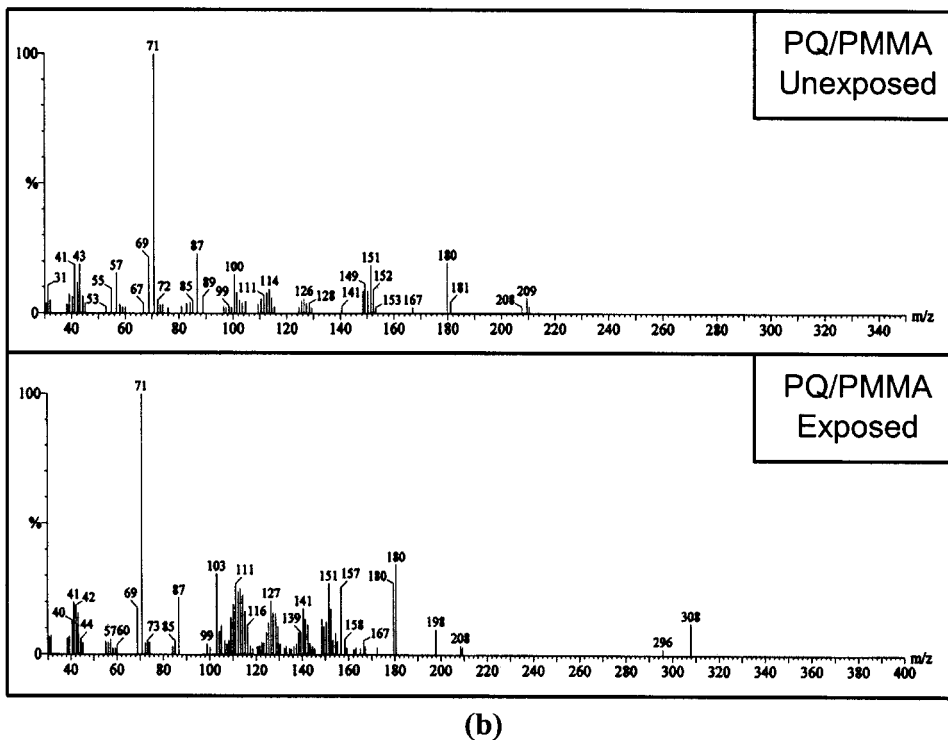
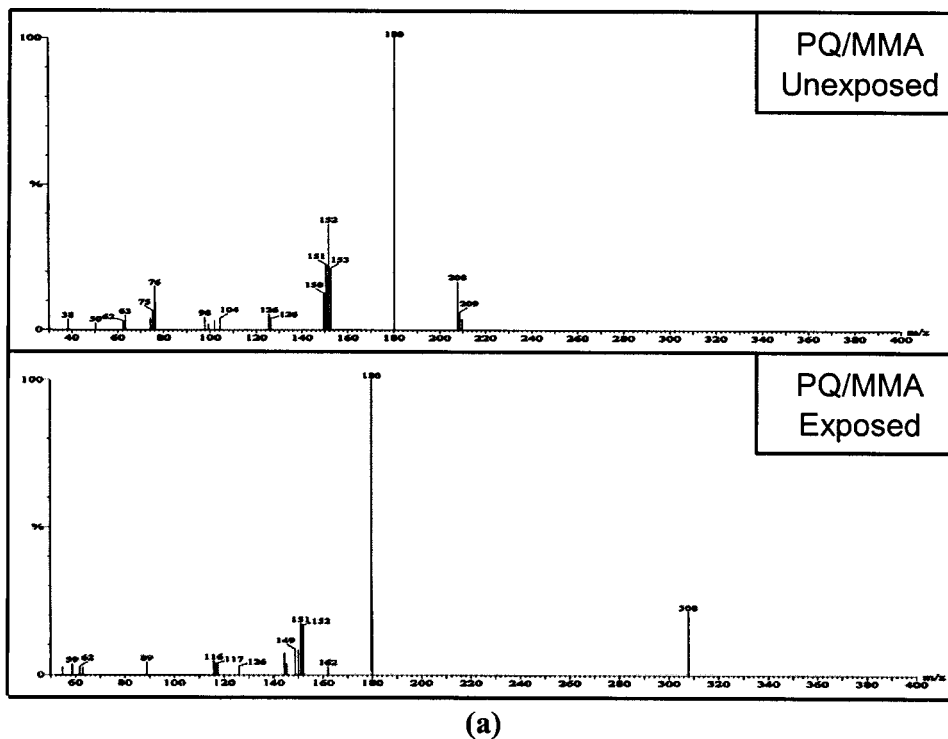


Fig. 5 The mass spectra of (a) an unexposed PQ/MMA liquid sample and photoproduct extracted from exposed PQ/MMA liquid sample, and (b) unexposed PQ/PMMA and exposed PQ/PMMA solid samples.

spreads between wave numbers 3000 cm^{-1} to 3100 cm^{-1} , as shown in Fig. 6(a), indicating the existence of C-H on an aromatic function group. For the MMA, a weak peak with wave-number spreads between 2800 cm^{-1} to 3000 cm^{-1} , as shown in Fig. 6(b), indicates the existence of C-H on an aliphatic function group. Similarly, Fig. 6(c) shows that the

photoproduct also has a weak peak in the same range. In Figs. 6(a), 6(b) and 6(c), no peaks appear at wave numbers higher than 3100 cm^{-1} . It implies that there is no OH functional group formed in the photoproduct. And so it is plausible to exclude the routes II and III from the possible photoreactions in Fig. 1.

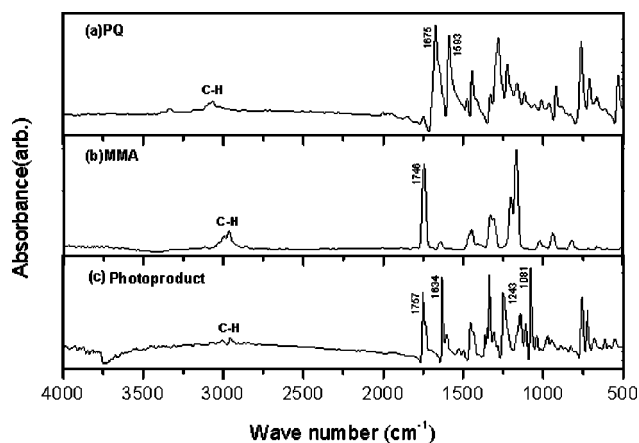


Fig. 6 The FT-IR absorption spectra of PQ, MMA, and photoproduct extracted from light-exposed PQ/MMA.

In the low wave-number regime of Fig. 6(a), we see two peaks occurring at 1675 cm^{-1} and 1593 cm^{-1} . These are due to the stretching energy of C=O and C=C in PQ molecules. In Fig. 6(b), the peak occurring at 1746 cm^{-1} is the absorption peak of C=O in MMA molecules. As for the photoproduct, we discuss four peaks in the same regime in Fig. 6(c). They are located at 1757 cm^{-1} , 1634 cm^{-1} , 1243 cm^{-1} , and 1081 cm^{-1} , respectively. The one at 1757 cm^{-1} is due to the absorption of C=O in the acrylate part of the photoproduct. Originally this signal is produced by absorption of C=O in MMA, corresponding to the 1746 cm^{-1} peak shown in Fig. 6(b). The second peak at 1634 cm^{-1} is produced by absorption of either C=O in the carbonyl group or C=C in the aromatic ring of the photoproduct. Originally the absorption peaks of these two bonds are separated and located at 1675 cm^{-1} and 1593 cm^{-1} in

Fig. 6(a), but two peaks are merged after light exposure. It can be seen that both new peaks are shifted from the original positions. It indicates that light exposure forms a new compound, such that function groups surrounding the C=O in MMA and the C=C in PQ have been changed. Therefore, the stretching and vibration energy of those bonds are changed such that their absorption peaks are shifted. In addition, we see that the absorption at 1634 cm^{-1} is partially contributed by the C=O of the photoproduct. It indicates that one of the carbonyl groups (C=O) of the PQ molecule may remain in the photoproduct and produce a shifted absorption peak in this range. These evidences provide only information to indicate that the light exposure has changed the function groups surrounding the C=O and C=C bonds. The possible routes, which are taken by new photoreactions, should be verified by new absorption peaks that appear in the spectra.

Two new peaks at wave numbers 1081 cm^{-1} and 1243 cm^{-1} , which are newly produced by the light exposure, indicate that light exposure has turned the carbonyl group on the PQ molecule and the vinyl group on the MMA molecule into an aromatic ester function group, C-O-C. This reaction is a photocyclo-addition, which occurs after PQ absorbs the photon energy. There are two possibilities for this reaction, which are indicated by path I and IV in Fig. 1.

Therefore, the results of FTIR spectra analyses suggest that by light exposure, PQ and MMA molecules in our sample react to form the one-to-one photoproduct by taking path I or IV in Fig. 1.

3.1.5 ^1H NMR spectra measurements

Figure 7 shows the ^1H NMR spectra of the photoproduct extracted from light-exposed PQ/MMA samples. Each peak

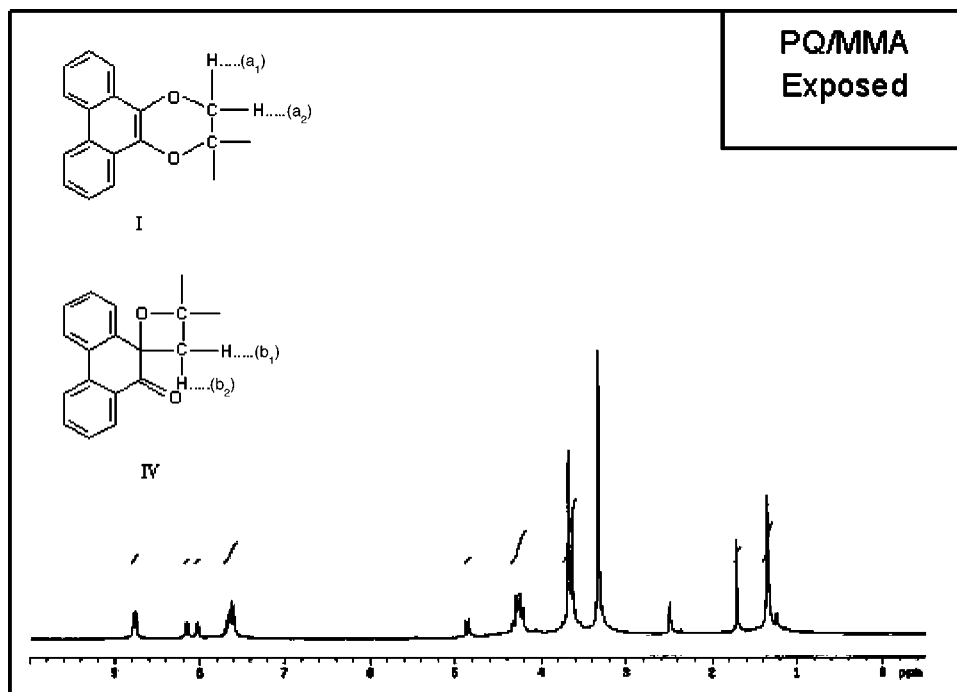


Fig. 7 The ^1H NMR spectra of photoproduct extracted from light-exposed PQ/MMA.

in the figure indicates the possible locations of hydrogen atoms and their surrounding functional groups in the molecule structure of the photoproduct. Those four peaks appearing between 7 to 9 represent the hydrogen atoms that are attached on the phenyl group, which originally are attached on the aromatic ring of the PQ molecule before exposure. It indicates that light exposure breaks only the carbonyl group of the PQ molecule.

Two peaks appearing between 4 and 5 represent two hydrogen atoms that are attached on an aromatic ester functional group of the photoproduct. They are originally located on the MMA molecule before exposure. Again, there are two possibilities for these new photoproducts, which are indicated by path I and IV in Fig. 1. They are similar in structure, so that these two hydrogen atoms in two vinyl functional groups should produce similar characteristic signal peaks in ^1H NMR spectra. To explain the results in detail, we label the two hydrogen atoms of the photoproduct of the path I compound as a1 and a2, and those of path IV as b1 and b2, respectively, as sketched in the left corner of Fig. 7. In principle, the hydrogen atoms of a2 and b2 will produce a signal peak at around 4.8. However, the two hydrogen atoms in the vinyl functional group of the compound are coupled such that the peak is split into two close peaks. Similarly, the hydrogen atoms a1 and b1 produced two more close peaks at around 4.2. Therefore, there are four separated peaks in the region between 4 and 5. This could be important evidence to show that there are two photoproducts coexisting in the light-exposed PQ/MMA sample, and both are formed by one PQ plus one MMA molecule.

Now we look at the regime with lower ^1H NMR spectra. There are very close double peaks appearing at 3.62 and 3.7. The peak at 3.62 is produced by the hydrogen atoms in the methyl group of photoproducts. Before exposure, these hydrogen atoms are originally attached on the methyl group of MMA molecules, which is close to the vinyl group. The peak at 3.7 is also produced by the hydrogen atoms in the methyl group of photoproducts. It implies that light exposure has induced two photoreactions. One is one-to-one attachment of PQ and MMA molecules. It gives the absorption peak at 3.62. The other is a PMMA polymer. Such polymer chains have many methyl functional groups surrounded by different functional groups, so that the signals produced by different hydrogen atoms in the different methyl functional groups are mixed and broadened. It appears at 3.7 with a broadened shape.

The peak at 3.3 is produced by the hydrogen atoms in water molecules. The water is absorbed from air by solvent d-DMSO. The peak at 2.49 is produced by the hydrogen atoms in solvent d-DMSO molecules. These two peaks are not important for analyzing the photoproduct.

Another example to indicate that both products coexist in our exposed sample are those peaks in the region between 1 and 2. The peak at 1.71 is produced by the hydrogen atoms in the methyl functional group of the ester side in the one-to-one photoproduct, and the peaks appearing at 1.4 are produced by that of the polymer chain. Again, we see that due to the polymerization of MMA molecules, the peak at 1.4 is broadened and the associated close peak appears at 1.2.

Table 1 Molecular weights of materials from GPC analyses.

Sample name	Mn	Mw	Polydispersity
Exposed PQ/MMA	612.6	1575.7	2.572
Unexposed PQ/PMMA	120365.1	270201.4	2.245
Exposed PQ/PMMA	196388.9	276022.6	1.405

Therefore, the ^1H NMR spectra provide us very useful information about the photoproducts in the exposed PQ/MMA samples. Both photoreactions of one-to-one attachment and photopolymerization have been observed. The one-to-one attachment could be formed by path I or IV in Fig. 1. The photoinduced polymerization could combine PQ with several MMA molecules to form an oligomer. This photoreaction can be further confirmed by the following GPC analyses.

3.1.6 Gel permeation chromatograph measurements

Table 1 summarizes the GPC measurement on the number-average molecular weight (Mn), the weight-average molecular weight (Mw), and the polydispersity (defined by Mw/Mn) for photoproducts extracted from light-exposed PQ/MMA, and unexposed and exposed PQ/PMMA samples. Here, the value of polydispersity indicates the degree of purity of the polymer molecule. If the value of polydispersity equals 1, the sample should be a highly pure polymer with a molecular weight of Mn. The larger the value is, the wider the polymer sample distribution of the molecular weight.

Consider first the photoproduct extracted from light-exposed PQ/MMA—the polydispersity is about 2.572. It implies that new photoinduced polymerization occurs in this sample. Also by comparing Mn, Mw, and polydispersity of the exposed PQ/MMA sample with the molecular weights of PQ (=208) and MMA (=100) molecules, we find that PQ and MMA molecules indeed carry out a little degree of photoinduced polymerization to form oligomers. This result confirms what has been observed in the NMR analysis: under light exposure, one PQ may link with four to several MMA molecules to form oligomers.

Then we consider the GPC analysis on exposed and unexposed PQ/PMMA. We find that the values of Mn and Mw are slightly different. Since in both samples the matrix PMMA is already polymerized and the concentration of the photoinduced oligomers is too small to affect the molecular weight of the sample, we cannot see a light-induced change of molecular weight of our sample. The difference of measured values between the exposed and unexposed samples is because we pick two different samples during the measurements. Although these two samples have the same parameters during sample preparation, the degrees of purity of the polymerization of the liquid samples are different. However, we find that the polydispersities of both samples are much larger than 1. This implies that both bulk samples are not completely polymerized and should contain some amount of unreacted MMA monomer to provide elements for holographic recording, which follows our design.

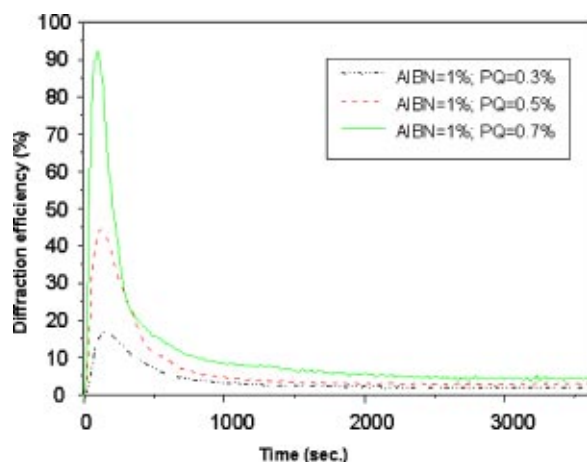


Fig. 8 The holographic recording dynamics of our photopolymer samples with different concentrations of PQ molecules.

3.1.7 Discussions

From the previous chemical analyses, it is clear that under light exposure the PQ molecules mainly react with residual MMA molecules by chemical paths I and IV, shown in Fig. 1, to form a one-to-one photoproduct in our PQ/PMMA photopolymer samples. The physical mechanism of holographic recording in our PQ/PMMA samples can be proposed as follows. During holographic recording, each photosensitive PQ molecule absorbs photons and bonds with one residual monomer molecule to become a radical structure. This photochemical reaction occurs in the bright region. Consequently, a difference in the refractive index in the dark region and that in the bright region is created, i.e., a phase grating is formed by the structure change of the PQ molecules. Since the monomers and photosensitizers involved in the formation of the holograms are only a small fraction of the material compositions, the host polymer matrix structure remains unaffected during the optical recording. As a result, the dimensional shrinkage and the bulk refractive index change induced by the holographic recording process are minimized. This mechanism can be applied to similar photopolymer materials such as molecules with o-quinone functional group in doped PMMA photopolymer. The holographic recording of our photopolymer materials are characterized in the next section.

3.2 Holographic Recording

We first write plane wave holograms in the PQ/PMMA samples 4.8 mm thick. Figure 8 shows the hologram diffraction efficiency as a function of exposure energy for samples with different PQ concentrations. It is seen that for all samples, the diffraction efficiency (the diffracted light intensity divided by the total light intensity transmitted through the sample) reaches a maximum value at the exposure energy of 0.3 J/cm^2 . The higher the concentration of PQ, the higher the maximum value of the diffraction efficiency. Further exposure causes the diffracted signal to drop. At this moment, the distortion in the geometrical shape of the transmitted beam has also been observed. The beam distortion and drop of diffraction efficiency are caused by the noise gratings produced by overexposure. The noise gratings are formed by the scattered beams,

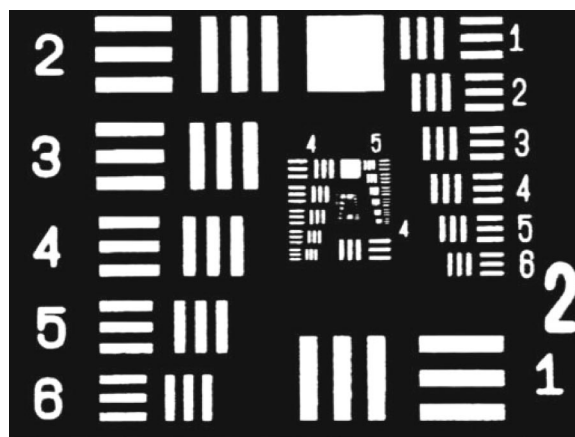


Fig. 9 The reconstructed resolution chart picture from the hologram.

which are produced by scattering centers such as micro air bubbles or the nonuniformity of the refractive index of the photopolymer. Because of the long interaction length in the bulk volume, the scattered beams interfere constructively to form noise gratings. The noise grating in turn enhances the nonuniformity of the refractive index of the photopolymer. Hence, when the noise gratings are strong, most of the energy of the incident light will be scattered and the diffracted beam is weakened and distorted. The implication of the growth of the noise grating is that there should be an upper limit to the exposure time for a single holographic recording; otherwise the noise grating will grow to deteriorate the recorded hologram.

To inspect the image quality of the holographic recording, we have recorded a Fresnel hologram in our sample using the resolution test chart. Figure 9 shows the photograph of the reconstructed image, in which the sample is placed near the Fourier plane of the imaging lens. It can be seen that the image retains clear fidelity, which is down to number 6 of group 5. This is equivalent to be the resolution of around 100 lps/mm. For volume holographic storage, thousands of pages are superimposed on a single location of a thick recording material. As the number of recording pages is increased, the diffraction efficiency of each hologram is very weak (typically less than 10^{-6}), and particular attention must be taken to keep material scattering noise to a minimum. Thus it is very important to grow a material with high uniformity. In this aspect, our technique of pre-polymerization during material fabrication seems to produce satisfactory uniformity of refractive index for multiple holographic storage.

Next, we characterize the dynamic range of our samples for multiple holographic recording. For multiplexed holographic storage, the amplitude of the grating strength of each hologram is proportional to the square root of the diffraction efficiency. A larger dynamic range of the material will give a higher diffraction efficiency of each hologram. The characteristic dynamic range of the material can be defined as the summation of cumulative grating strength of the recorded holograms at one location,^{19,20} which is called the $M/\#$, i.e.,

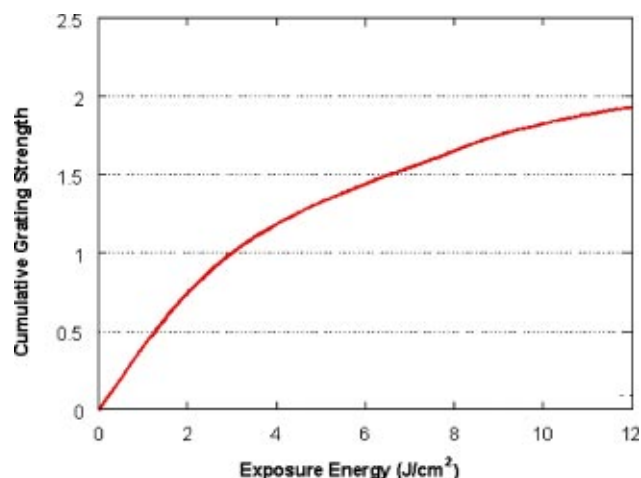


Fig. 10 The running curve of the cumulative grating strength for a photopolymer sample with thickness of 1 mm.

$$M/\# = \sum_{i=1}^N \sqrt{\eta_i} \quad (1)$$

where N is the total number of holograms recorded at one location until the material is exhausted. To characterize the $M/\#$ of our samples, we have performed a hologram recording using the technique of peristrophical multiplexing.²¹ 300 plane wave holograms, each with equal exposure energy ($\sim 40 \text{ mJ/cm}^2$), were recorded at a single location of the polymer sample. After recording, the diffraction efficiency of each hologram was measured, and the square roots of the diffraction efficiencies were summed up to obtain a running curve of the cumulative grating strength (defined as

$$C = \sum_{i=1}^M \sqrt{\eta_i}$$

where M is the total number of holograms that have been recorded) as a function of the cumulative exposure energy. The running curve for different polymer samples with thickness of 1.0 mm is given in Fig. 10. According to Eq. (1), the saturation value of the cumulative grating strength is equal to the $M/\#$. From Fig. 10, the $M/\#$ of our PQ-doped PMMA is around 2 mm^{-1} . Our further experiments show that the $M/\#$ grows linearly with the thickness of the samples. Furthermore, the characteristic exposure sensitivity, which is defined as the necessary energy for the value C to reach around 63% of the saturated value, can be estimated by an exponential curve fitting of the running curves in Fig. 10. It can be calculated that the characteristic exposure sensitivity of our PQ-doped PMMA samples is $\sim 4.76 \text{ J/cm}^2$. According to the diffraction formula of a volume phase grating, the saturated refractive index change of photopolymers can be estimated to be 3.25×10^{-4} .

4 Conclusions

To identify the photoproducts in our PQ/PMMA samples, different chemical analyses are performed in PQ-solved MMA liquid and PQ-doped PMMA solid samples, both

with unexposed and exposed cases. The FT-IR spectra show that no OH functional groups are left in the exposed samples. This result excludes the possibilities of photochemical reaction paths II and III shown in Fig. 1. The mass spectra indicate that under light exposure, a new compound based on one PQ molecule and one MMA molecule is produced. Measurements of PL spectra confirm that under light exposure, the C=O bond of PQ is attached with C=C of MMA. From these analyses, we conclude that photoreaction should take place by paths I and IV shown in Fig. 1. The $^1\text{H-NMR}$ spectra indicate that there is photoinduced polymerization process in our photopolymers beside one-to-one attachment. The GPC analyses further confirm that an oligomer is formed as PQ/MMA solution is exposed in green light. It indicates that under light exposure, PQ molecules function as photoinitiators to become free radicals, which combine with MMA molecules to form oligomers. The holographic recording mechanism in our PQ/PMMA photopolymer is mainly due to the structural change of PQ molecules, resulting in a strong change in the refractive index of a material. It provides the possibility to record phase holograms with negligible shrinkage effects. The holographic recordings in those samples is demonstrated. Our technique of prepolymerization during material fabrication seems to produce a satisfactory uniform refractive index for holographic storage. By measuring the recording dynamics of multiple holograms in these photopolymer samples, the characteristics of our material are investigated. The criteria for evaluating the dynamic range and sensitivity for holographic recording, defined as the $M/\#$ and characteristic exposure energy of the polymer, respectively, are described. The results show that the $M/\#$ can be as large as 2.06, and its characteristic exposure sensitivity can be as small as 4.76 J/cm^2 for 1-mm-thick samples. This $M/\#$ value corresponds to the refractive change in our photopolymer to be 3.25×10^{-4} . The results can be extended to different o-quinone-based molecules in doped PMMA hybrid materials.

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References

1. D. Psaltis and F. H. Mok, "Holographic memories," *Sci. Am.* **273**(5), 70–76 (1995).
2. H. J. Coufal, D. Psaltis, and G. Sincerbox, *Holographic Data Storage*, Springer Verlag, New York (2000).
3. B. L. Booth, "Photopolymer material for holography," *Appl. Opt.* **14**(3), 593–601 (1975).
4. F. P. Laming, *Polym. Eng. Sci.* **11**, 421–425 (1971).
5. H. Franke, "Optical recording of refractive-index patterns in doped poly-(methyl methacrylate) films," *Appl. Opt.* **23**(16), 2729–2733 (1984).
6. U. S. Rhee, H. J. Caulfield, C. S. Vikram, and J. Shamir, "Dynamics of hologram recording in DuPont photopolymer," *Appl. Opt.* **34**(5), 846–853 (1995).
7. K. Y. Hsu, S. H. Lin, W. T. Whang, and W. Z. Chen, "Holographic data storage using photopolymers," *Proc. SPIE* **3801**, 66–74 (1999).
8. M. L. Hsieh and K. Y. Hsu, "Grating detuning effect on holographic memory in photopolymers," *Opt. Eng.* **40**(10), 2125–2133 (2001).
9. L. Dhar, A. Hale, H. E. Katz, M. L. Schilling, M. G. Schnoes, and F. C. Schilling, "Recording media that exhibit high dynamic range for digital holographic data storage," *Opt. Lett.* **24**(7), 487–489 (1999).

10. A. Pu and D. Psaltis, "High-density recording in photopolymer-based holographic three-dimensional disks," *Appl. Opt.* **35**(14), 2389–2398 (1996).
11. X. Yi and P. Yeh, *CLEO/Pacific Rim '99* **4**, 1175–1176, IEEE Press (1999).
12. G. J. Steckman, I. Solomatine, G. Zhou, and D. Psaltis, "Characterization of phenanthrenequinone-doped poly(methyl methacrylate) for holographic memory," *Opt. Lett.* **23**(16), 1310–1312 (1998).
13. S. H. Lin, K. Y. Hsu, W. Z. Chen, and W. T. Whang, "Phenanthrenequinone-doped poly(methyl methacrylate) photopolymer bulk for volume holographic data storage," *Opt. Lett.* **25**(7), 451–453 (2000).
14. J. Mumbru, I. Solomatine, D. Psaltis, S. H. Lin, K. Y. Hsu, W. Z. Chen, and W. T. Whang, "Comparison of the recording dynamics of phenanthrenequinone-doped poly(methyl methacrylate) materials," *Opt. Commun.* **194**(1–3), 103–108 (2001).
15. S. Farid, D. Hess, G. Pfundt, K. H. Scholz, and G. Steffan, "Photo-reactions of *o*-quinones with olefins: a new type of reaction leading to dioxole derivatives," *Chem. Commun. (Cambridge)* **434**(5), 638–639 (1968).
16. See <http://www.sigmaaldrich.com>
17. See <http://www.st.rim.or.jp/~shw/alphable.html>
18. See <http://www.lancastersynthesis.com>
19. F. Mok, G. Burr, and D. Psaltis, "System metric for holographic memory systems," *Opt. Lett.* **21**(12), 896–898 (1996).
20. A. Pu, K. Curtis, and D. Psaltis, "Exposure schedule for multiplexing holograms in photopolymer films," *Opt. Eng.* **35**(10), 2824–2829 (1996).
21. K. Curtis, A. Pu, and D. Psaltis, "Method for holographic storage using peristrophic multiplexing," *Opt. Lett.* **19**(13), 993–994 (1994).



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