1 Introduction

Holographic data storage has been considered a promising information storage technology because of its large storage capacity and inherent property of parallel data recording and retrieval.\(^1\) It is known that in order to achieve high storage density, thousands of data pages should be superimposed in the same spatial location of a storage volume by a multiplexing scheme using Bragg selectivity of thick holograms.\(^2\) To accomplish this type of volume hologram recording, a recording material of several-millimeters thickness that can produce high photoinduced refractive index change is required. Furthermore, dimensional stability of the volume hologram is necessary. Otherwise, the material shrinkage during holographic recording will induce a mismatch of Bragg condition for volume holograms such that the recorded information cannot be retrieved completely.\(^3\) Several photocopolymer materials with low photoinduced shrinkage have been developed for write-once materials.\(^4\)\(^-\)\(^6\) In our laboratory, we have developed a technique for fabricating phenanthrenequinone-doped poly(methyl-methacrylate) (PQ/PMMA) photopolymer that is 1-cm thick and has negligible photoinduced shrinkage.\(^7\)\(^-\)\(^9\) Holographic experiments using these PQ/PMMA samples have showed that the coefficient of photoinduced shrinkage in this material is less than 10\(^{-5}\), so our samples are especially attractive for volume hologram applications.\(^1\)\(^1\)

However, because of the solubility of the doped element, in this case PQ, in the polymer matrix is low, the concentrations of chemical elements for holographic recording are limited. Thus, when compared with other materials, the drawback in our PQ/PMMA is lower sensitivity and smaller dynamic range of recording. To further improve the material, investigations on the physical mechanism of holographic recording in PQ/PMMA have been performed.\(^1\)\(^2\)\(^-\)\(^5\)\(^1\)\(^2\)\(^-\)\(^1\)\(^5\) The investigations reveal that under illumination, photons excite the quinone double bond on the carbonyl functional group of PQ molecules, and PQ molecules become radicals. Then, the radical reacts with the carbonyl double bond on the vinyl functional group of the MMA molecule to form a new compound. In this chemical reaction, the double bond of the vinyl group has been converted to a single bond such that the change in bond order contributes to a significant change in molar refraction and then the refractive index of material is changed, as indicated by Tomlinson and Chandross.\(^1\)\(^6\) They estimated the refractive change for the vinyl monomers to be an order of magnitude of 10\(^{-2}\). Thus, a refractive-index pattern of the material follows that of the light intensity, and a phase hologram is then formed.

In this paper, we apply this knowledge to improve the PQ/PMMA photopolymer. Our strategy is to enhance the combination probability of monomer molecules with PQ radicals. This may be achieved by increasing the number of vinyl functional groups on the monomer, and/or by changing the side functional group of the vinyl group on the monomer. To accomplish this goal, we chose two different monomers, trimethylolpropane triacrylate (TMPTA), which has three vinyl groups, and 2-phenoxyethyl acrylate (PEA), which has an additional benzene side functional group. Figure 1 shows their chemical formulas. However, these two monomers do not easily form a hard polymer matrix.\(^1\)\(^7\) Thus, a copolymer technique is used here. Each of the two monomers forms a copolymer matrix system with MMA at a weight ratio of 4:1. Thus, two novel PQ-doped copolymer samples have been fabricated, both with 2-mm thickness.

In Sec. 2, we first describe the fabrication of these two copolymer materials. Then, chemical analyses of the
samples before and after light exposure are investigated, and a physical mechanism of holographic recording is presented. Section 3 gives the holographic recording characteristics, including dynamic range and sensitivity, of different samples. In Sec. 4, we discuss the experimental results and propose a modified fabrication procedure of the sample to further enhance holographic characteristics of the materials. The results show that an improvement of holographic characteristics of PQ/PMMA can be achieved through the copolymer technique. Section 5 gives conclusions.

2 Material Fabrication and Analyses

2.1 Sample Fabrications

First, saturated concentration (~0.7 wt%) of photosensitizer, PQ, and 1 wt% of thermal initiator, 2,2-azo-bis-isobutylornitrile (AIBN) molecule, were dissolved in a mixture solution of monomer liquid, which is a mixture of monomer components for the copolymer matrix, MMA plus PEA, or MMA plus TMPTA. These monomer components were mixed at a weight ratio of 4 to 1: MMA to PEA=4:1 and MMA to TMPTA=4:1. The resulting solution was placed in an ultrasonic water bath at 30 °C for 1 h, until all the components were dissolved completely. The solution was purified to remove the undissolved particles so as to reduce light scattering centers. The purified solution was stirred (using a magneto stirrer) in an open-end glass bottle at 30 °C for an appropriate period of time. At this fabrication step, one could observe that the liquid solution became thicker and thicker as a result of the polymerization reaction. Thus, the viscosity of the solution is a good indicator of the degree of polymerization. Viscosity measurements with a typical capillary instrument provide useful information for the decision of when to proceed to the step for molding. Table 1 lists the stirring time for different mixtures, respectively, to reach a similar viscosity. As illustrated in Table 1, the solution mixture of MMA and TMPTA needs the shortest stirring time. It implies that more vinyl groups in TMPTA molecules can accelerate the polymerization rate. On the other hand, we observe that the solution mixture of MMA and PEA needs the longest stirring time. This indicates that the benzene side functional group on the PEA monomer may not be easily infixed into the copolymer matrix.

After the stirring, the viscous solution was poured into a glass container with a 2-mm thick spacer. The thickness and geometrical shape of the sample was determined by the geometry of this container. The sample was then baked at 45 °C for 72 h, until most of the monomers were polymerized, and then the liquid sample had been transferred into a self-sustained solid block. The sample could be removed from the mold for optical and holographic characterizations. Hereafter, the samples of PQ doped in the polymer system of PMMA, the copolymer system of TMPTA and MMA, and the copolymer system of PEA and MMA are named as PQ/PMMA, PQ/poly-(TMPTA-co-MMA), and PQ/poly-(PEA-co-MMA) photopolymers, respectively.

2.2 Analyses on Photochemical Reaction

To understand the photoinduced chemical reactions in these samples, we performed mass spectrum measurement of the samples before and after an optical exposure. These spectra provide information about the molecular weight distribution of the compounds in material and will reveal whether there is any new compound produced by the light exposure. Because our photopolymers were sensitive to green light, the samples were illuminated with a 514-nm argon laser beam until they were optically saturated (which means becoming transparent). Figure 2 shows mass spectra of the three samples. As can be seen in Fig. 2(a), a new characteristic peak signal at 308 gives evidence that the photoproduct 296, which is the molecular weight of TMPTA molecule, was formed by attachment of one MMA molecule to one PQ mole in PQ/PMMA, as was pointed out in our previous work.

Figure 2(b) shows the measurement result for PQ/poly-(TMPTA-co-MMA) sample. In the mass spectrum of the unexposed sample, we cannot find a peak signal at around 296, which is the molecular weight of TMPTA molecule. This indicates that in PQ/poly-(TMPTA-co-MMA) only one species of residual monomer, MMA is left in this polymer matrix. This can be attributed to the high activity provided by the three vinyl groups, such that almost all TMPTA monomers participated to form the polymer matrix during sample fabrication. Thus, there will be only residual MMA monomers for holographic recording. On the other hand, for the exposed sample in the large molecular weight

![Trimethylolpropane Triacrylate (TMPTA)](image)

![2-Phenoxyethyl Acrylate (PEA)](image)

**Table 1** The stirring time for different mixtures to reach a similar viscosity.

<table>
<thead>
<tr>
<th>Name</th>
<th>Stirring time (h)</th>
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<tbody>
<tr>
<td>PQ/PMMA</td>
<td>24</td>
</tr>
<tr>
<td>PQ/poly-(PEA-co-MMA)</td>
<td>48</td>
</tr>
<tr>
<td>PQ/poly-(TMPTA-co-MMA)</td>
<td>6</td>
</tr>
</tbody>
</table>
The mass spectra of unexposed and exposed states of the PQ/poly-(PEA-co-MMA) sample, which is the same as that in the PQ/PMMA sample. Furthermore, it can also be observed that several new peaks appear after exposure. Among them, signals at 308 and 400 are interesting for identifying the photoproduct. Because the molecular weight of PEA is 192, this result indicates that two kinds of the photoinduced attachments occur during light exposure: one PQ molecule to one residual MMA monomer and one PQ molecule to one PEA monomer.

Accordingly, Fig. 2 reveals an important message about light-induced chemical reaction in these three samples: a new compound has been formed, of which the molecular weight equals to the summation of one PQ plus one residual monomer. This photoproduct can be attributed to the attachment of one PQ molecule to one residual monomer molecule. On the other hand, there is no indication about the participation of the polymer matrix on the photochemical reaction. This implies that the physical mechanism of holographic recording in all these samples follows our design strategy:10 light exposure will not cause any change to the polymer matrix. Thus, samples could retain an important characteristic for volume holographic recording: minimum photochemical-shrinkage effect.

3 Holographic Characterizations

3.1 Holographic Recording in the Samples

To test the hologram recording capability of our photopolymer samples, we have recorded a plane-wave hologram in each sample. A s-polarized beam from an argon laser with wavelength 514 nm was collimated and split into two beams. Each beam had the intensity of 30 mW/cm², and the two beams were incident into the sample symmetrically with an intersection angle of 30 deg in the air. During recording, the diffraction efficiency, which is defined as the ratio of the diffracted intensity to the summation of diffracted and transmitted intensities, was measured in real time by use of a weak helium-neon laser illuminated at the Bragg-matched angle. Diffraction efficiency for each sample was plotted as a function of exposure energy, as shown in Fig. 3. As indicated by the curve with symbol ■, it is seen that the diffraction efficiency of PQ/PMMA first reaches 100% at the exposure energy of 2.5 J/cm² and then it begins to drop with further exposure. The drop-off in diffraction efficiency is attributed to two effects: the backward coupling of the diffracted beam to the transmitted beam in the beginning and the fanning of noise gratings further. These noise gratings were formed by scattering in the material and then took out the power of the incident beam such that the diffraction efficiency of the hologram is reduced.13 In this case, the refractive index change Δn of grating calculated from diffraction efficiency is meaningful in the beginning regime of the hologram recording. It is estimated to be 1.27 × 10⁻⁴ when the diffraction efficiency reaches to 100%.

Copolymer samples PQ/poly-(TMPTA-co-MMA) and
PQ/poly-(PEA-co-MMA) both exhibit similar temporal behaviors of diffraction efficiency, as indicated in Fig. 3 by curves with symbols △ and ○, respectively. It is seen that both the copolymers possess a larger rising slope during the first regime of hologram recording (exposure < 2 J/cm²). Thus, addition of either TMPTA or PEA monomer molecules into the PQ/PMMA photopolymer could help to improve the recording sensitivity of the material. Among them, the PQ/poly-(PEA-co-MMA) sample has faster holographic recording speed.

### 3.2 Characterizing Material for Holographic Data Storage

The $M$-number ($M#$) and sensitivity ($S$) are the two typical parameters that have been used to characterize a holographic recording media for data storage. The two parameters can be obtained experimentally by multiplexing a series of plane-wave holograms at a single spot in the sample until the material is chemically exhausted. After recording, the diffraction efficiency of each hologram was measured. The summation of the square roots of the diffraction efficiency of each hologram, named as the cumulative grating strength, forms a running curve of cumulative refractive-index change function, $C(E)=\sum_{i=1}^{n}\eta_i$, where $n$ is the total number of holograms that have been recorded at the cumulative exposure energy $E$. The saturation value of the cumulative grating strength gives $M#$. This running curve also indicates the build-up dynamics of the multiple hologram recording. According to the definition, the material sensitivity can be represented as change of the cumulative refractive index change divided by the corresponding exposure energy of that hologram, $S=\Delta C(E)/\Delta E_{\text{one hologram}}$.

We have recorded 175 holographic exposures at one spot of each material with a peristrophic multiplexing system, in which each exposure had equal exposure energy 0.23 J/cm². The running curves of cumulative refractive-index change for different samples are shown in Fig. 4. If we perform a curve fitting by the function: $C(E)=C_{\text{sat}} \exp\left[1-\left(\frac{E}{E_s}\right)^n\right]$, then the $M#$ (i.e., $C_{\text{sat}}=M#$) and an expenditure energy constant $E_s$ of the material are obtained. From these results, sensitivity of the fresh samples can be found to be given by:

$$S = \frac{dC(E)}{dE} \bigg|_{E=0} = \frac{M#}{E_s}.$$  

Using the above formulas, the material $M#$ and $E_s$ of the three samples are obtained and listed in Table 2. First, it can be seen in the table that the $M#$ of PQ/poly-(PEA-co-MMA) is 4.05, which is 1.5 times larger than that of PQ/PMMA ($M# \sim 2.85$). On the other hand, the $M#$ of PQ/poly-(TMPTA-co-MMA) is slightly less than that of PQ/PMMA. Then, as shown in the last column in Table 2, $S$ of the copolymers are 0.39 and 0.61 cm²/J, which have been improved from that of PQ/PMMA by about 1.3 and 2 times, respectively. The results indicate that by adding additional monomer components to form the copolymer structure, holographic recording characteristics of a PQ-doped photopolymer can be improved.

### 4 Discussion

As was presented in the previous paragraph, both $M#$ and $S$ have been improved in PQ/poly-(PEA-co-MMA), whereas in PQ/poly-(TMPTA-co-MMA), only $S$ had been improved slightly and $M#$ was even reduced on the contrary. The experimental results seem to be not completely consistent.

<table>
<thead>
<tr>
<th>Name</th>
<th>PQ/PMMA</th>
<th>PQ/Poly-(PEA-co-MMA)</th>
<th>PQ/Poly-(TMPTA-co-MMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M#$</td>
<td>2.85</td>
<td>4.05</td>
<td>2.75</td>
</tr>
<tr>
<td>$E_s$ (J/cm²)</td>
<td>9.17</td>
<td>6.61</td>
<td>7.02</td>
</tr>
<tr>
<td>$S$ (cm²/J)</td>
<td>0.31</td>
<td>0.61</td>
<td>0.39</td>
</tr>
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</table>
with our design strategy. However, this behavior can be understood by inspecting the mass spectrum of the copolymer samples, shown in Fig. 2.

In Fig. 2(c), mass spectra peaks appear at 99, 192, and 208 before optical exposure, indicating the availability of MMA, PEA, and PQ molecules for holographic recording. In the spectrum of sample after exposure, presence of peak signals at 308 and 400 indicates the occurrence of photoinduced chemical reactions of one PQ plus one MMA, and one PQ plus one PEA, respectively. This behavior is consistent with our design strategy of providing an additional functional group PEA for enhancing the photochemical reactions. This could explain the improvements of both M# and S in PQ/poly-(PEA-co-MMA).

On the other hand, in Fig. 2(b), the characteristic peak of TMPTA monomer at 293 was not observed before exposure, whereas a peak signal at 308 appears only after exposure. This implies that only PQ and MMA and no TMPTA are available in the sample before exposure, and indeed one PQ plus one MMA was the only photochemical reaction that occurred during the optical exposure. Thus, there were no residual TMPTA monomers in the copolymer sample, so that the holographic recording of this material was not improved.

These results indicate that to realize our design strategy of enhancing the photochemical reaction via providing more active functional groups, we have to improve the fabrication technique. Further, if a certain portion of TMPTA monomers can be retained in the copolymer matrix, then stronger photochemical reactions between PQ, MMA, and TMPTA can be obtained, and thus M# and S might be improved accordingly.

4.1 Copolymer Sample Fabricated With a Modified Procedure

We proposed to modify the fabrication procedure so that a certain portion of additional highly active monomers such TMPTA and PEA can be retained unpolymerized. These residual monomers could be used for the photochemical reaction during holographic recording. Our method is to control timing for adding PEA or TMPTA molecules to the solution during sample preparation.

With the modified fabrication procedure, we first mixed up the saturated concentration of photosensitizer, PQ, 1 wt% of thermal initiator, AIBN molecule and liquid MMA monomers. The resulting solution was stirred at 30 °C for 1 h until all components were dissolved completely. The solution continued to be stirred at 30 °C for another 24 h until it became viscous. At the same time, we prepared the PEA (or TMPTA) monomer solution with a saturated concentration of PQ molecules. The two solutions were mixed and stirred. The weight ratio of MMA and PEA (or TMPTA) is controlled to be 4:1. The mixed solution was poured into a glass container with a 2-mm thick spacer. It was baked at 45 °C for 72 h to form a bulk sample. For comparison, we also prepared a PQ/PMMa sample with the same procedure.

4.2 Mass Spectra Measurement

To analyze the species of the residual monomers and the photoproducts, we measured the mass spectra of the new samples before and after light exposure. Figure 5(a) illustrates experimental results for PQ/poly-(PEA-co-MMA). We observe that characteristic peaks of PQ, PEA, and MMA molecules appear at 208, 192, and 100, respectively, in the unexposed sample. It indicates that these three components are available in the unexposed sample. The bottom plot in Fig. 5(a) shows that characteristic peaks appear at 308 and 400 in the exposed sample, which correspond to the molecular weights of one PQ plus one MMA, and one PQ plus one PEA, respectively. Thus, the photoproducts in this sample are formed by the attachment of one PQ to either one MMA or one PEA molecule, which is the same as that in the old sample.

Similarly, in Fig. 5(b), for PQ/poly-(TMPTA-co-MMA) it can be seen that three characteristic peaks appear at 100, 208, and 293 in the unexposed sample. The molecular weights of 100 and 208 correspond to MMA and PQ molecules, respectively. Because the molecular weight of TMPTA is 296, the peak at 293 should correspond to the TMPTA by losing three hydrogen molecules. Thus, PQ...
We have performed a multiplexing holographic recording on the new samples. Sixty-five plane-wave holograms have been recorded in each sample, in which each hologram was recorded with equal exposure energy of 0.32 J/cm². The running curves for the build-up dynamics of multiple-hologram recording in these samples are shown in Figure 6. The material $M_\#$ and $E_\tau$ of the materials are obtained by curve fitting, and the sensitivities are calculated. The results are listed in Table 3. Comparing this table with Table 2, it is seen that holographic characteristics of these new samples have been improved. The sensitivity of new PQ/PMMA is around 2 times that of the original PQ/PMMA. The sensitivity of new PQ/poly-(PEA-co-MMA) is about 1.3 times that of the original PQ/poly-(PEA-co-MMA). The improvements in these two samples are due to the increase of retained monomers by using the modified fabrication technique. The most striking result is that the $M_\#$ and the sensitivity of new PQ/poly-(TMPTA-co-MMA) are 7.01 and 0.97. Compared with the original PQ/PMMA, the $M_\#$ and the sensitivity of the newly fabricated PQ/poly-(TMPTA-co-MMA) have been enhanced by a factor of 2.5 and 3.13 improvement, respectively. Holographic experimental results together with the mass spectra analyses show the modified fabrication technique is an effective way to retain TMPTA monomers in PQ/poly-(TMPTA-co-MMA) samples. These residual monomers are helpful to provide considerable improvements of dynamic range and sensitivity for holographic recording.

### Table 3: The fitting parameters of the running curve in the three samples fabricated using the new preparation method.

<table>
<thead>
<tr>
<th>Name</th>
<th>PQ/PMMA</th>
<th>PQ/Poly-(PEA-co-MMA)</th>
<th>PQ/Poly-(TMPTA-co-MMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_#$</td>
<td>3.35</td>
<td>4.98</td>
<td>7.01</td>
</tr>
<tr>
<td>$E_\tau$ (J/cm²)</td>
<td>5.63</td>
<td>6.3</td>
<td>7.27</td>
</tr>
<tr>
<td>$S$ (cm²/J)</td>
<td>0.6</td>
<td>0.79</td>
<td>0.97</td>
</tr>
</tbody>
</table>

**5 Conclusions**

We have fabricated and characterized PQ/PMMA and two kinds of PQ-doped copolymer samples, PQ/poly-(PEA-co-MMA) and PQ/poly-(TMPTA-co-MMA). We have performed mass spectra analyses of the samples before and after light exposure. The results indicate that for all of the PQ-doped samples light exposure induces photoproducts made of one PQ molecule plus one residual monomer. The results indicate that the physical mechanism of holographic recording in these samples follows our design strategy to minimize the photochemical-shrinkage effect. We have measured the holographic recording characteristics of these samples. The results show that both the $M_\#$ and the exposure sensitivity $S$ have been improved by about 1.5 to 2 times by introducing additional monomer into PQ/PMMA to form copolymer structures. The mass spectra analyses show that our fabrication method would not allow to keep all TMPTA from participating the polymerization reaction in the PMMA matrix during fabrication, and so the holographic improvement was restricted. We found that the timing for introducing reactive components into the monomer solution during fabrication provides one flexibility to improve the situation. For this, we have developed a new fabrication method, in that by controlling the timing for adding the reactive monomers into the solution matrix, a certain portion of TMPTA monomers can be preserved as residual monomers in a polymer matrix. The holographic...
characteristics have been further improved another 1.5 to 2 times. The results confirm that our design strategy fabricates large dynamic, highly sensitive, thick recording photopolymer materials with low shrinkage effect for holographic data storage.

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