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Preparation and characterization of Irgacure 784 doped photopolymers for holographic data storage at 532 nm

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Abstract

This paper presents the development of a thick photopolymer for holographic data storage at a wavelength of 532 nm. Irgacure 784, one kind of the titanocene photoinitiators, has been selected and doped to synthesize the photopolymers in this research. Using a two-step thermo-polymerization procedure two photopolymer samples have been fabricated, Irgacure 784 doped poly(methyl methacrylate) (PMMA) and Irgacure 784 doped epoxy resin. Samples of 2 mm thick have been fabricated. Holographic measurements show that Irgacure 784 doped epoxy resin is very sensitive at 532 nm and that it is capable of supporting holographic data storage at an ultra-fast recording rate of 760 Mb s⁻¹. Mass spectrum measurement, solid state ¹H-NMR spectrum measurement, and thermogravimetry analyses (TGA) have been performed. The results reveal the physical mechanism of holographic recording in these samples, providing a guideline for a design strategy and fabrication technique to produce a low-shrinkage recording material for holographic data storage in the tera-byte information age.

Keywords: holography, volume holographic material, photopolymer, poly(methyl methacrylate), epoxy resin

1. Introduction

Volume holography using thick recording materials is considered as a potential candidate for future 'ultra' storage technologies, because its three-dimensional structure facilitates terabyte (TB) storage capacity and the page oriented format allows one to achieve gigabyte (Gb) s⁻¹ data write and read rate [1]. Currently, this technology is on the horizon for commercial applications, but is still rich for research activities [2]. Among the various aspects, finding a suitable volume holographic material is the most important issue. For a long time, photorefractive crystals such as LiNbO₃ were almost exclusively used in research [3]. More recently, photopolymer materials have become more attractive, because their fabrication is less involved and costly. Modifying the material components and fabrication procedures is simpler.

The three most important parameters for evaluating a recording material for holographic data storage are: the dynamic range (or $M\#$ [4, 5]) for hologram recording, the sensitivity S for optical exposure, and a photo-induced material shrinkage coefficient during hologram recording. The specifications that are actually required are related to the performance parameters of the peripheral devices, such as the sensitivity of the photo-detector array (usually, CCD is used), the pixel number of the input spatial light modulator (SLM), and the available light power from a laser source. For example, if a CCD device with sensitivity of 10 000 electrons/pixel, an SLM with resolution of 1 Mbit per page, and a laser source with 100 mW are used in the system, and if we want to achieve 500 GB storage capacity on a 5 inch diameter disk with a Gb s⁻¹ data write/read rate, then it can be estimated that we require a holographic material with dynamic range $M\# = 28$ and sensitivity $S = 35 \text{ cm}^2 \text{ J}^{-1}$ [6].

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Actually, these requirements for the dynamic range and sensitivity are not difficult to meet with current photopolymer materials. The difficult part is the photo-induced shrinkage problem during hologram recording. As is well known, high storage capacity of holographic data storage arises from the Bragg selectivity of volume holograms, which allows the multiplexing of thousands of holograms into one location of the material. Even a small shrinkage during holographic recording could induce dimensional distortions of the recorded gratings, and that will lead to a mismatch of the Bragg condition in volume gratings such that the recorded information cannot be completely retrieved. This phenomenon becomes more severe as the material thickness is increased. For a recording material of 5 mm thick, it was estimated that the shrinkage coefficient should not exceed 5×10^{-5} [7].

In order to avoid the shrinkage problem, several fabrication methods have been proposed and investigated, including the doped system [8–11], sol–gel system [12–14], cationic ring opening polymerization system [15–19], organic–inorganic hybrid system [20–25] and crosslinked matrix system [26–28]. In our laboratory, we have developed a thermo-polymerization technique to fabricate dye doped poly(methyl methacrylate) (PMMA) photopolymer system. Bulk volume materials of mm to cm thickness with negligible shrinkage effect have been fabricated and tested [7, 29–31]. A series of quinone-based dye doped poly(methyl methacrylate) photopolymers have been fabricated and characterized [29]. Holographic experiments using these materials with an argon laser at wavelength 514 nm demonstrate that $M\#$ of 5.18, S of $1.6 \text{ cm}^2 \text{ J}^{-1}$, and shrinkage coefficient smaller than 10^{-5} have been achieved. According to the system evaluation, this material can support a holographic disk of storage capacity of 92.5 GB and data recording rate at 45 Mb s^{-1} . Though these characteristics are still far way from that required for the Tera-storage capacity and Giga-data rate, they are good enough for prototyping of holographic data storage. However, in order to develop a practical system, a compact diode-pumped solid state (DPSS) laser at 532 nm or a semiconductor laser at blue wavelengths should be used. Thus, holographic materials should be able to work at these wavelengths and with good characteristics for holographic experiments.

The main purposes of this research are, first, to investigate the characteristics of our quinone-based dye doped PMMA photopolymers for holographic data storage at 532 nm, and second, to investigate new photopolymers with improved holographic characteristics.

In section 2, by measuring the $M\#$ and S of the material, we investigate the suitability of one of our quinone-based dye doped photopolymers: 9,10-phenanthrenequinone doped poly(methyl methacrylate) (PQ/PMMA) for holographic data storage at 532 nm. The physical mechanism of holographic recording in PQ/PMMA will be briefly reviewed, and a method for the material's improvement will be presented. Section 3 presents the fabrication and holographic experiments of a new Irgacure 784 doped PMMA photopolymer. The physical mechanism of holographic recording in this material will be investigated, and a strategy for improving the material will be described. Section 4 describes the fabrication and holographic

characterization of a new Irgacure 784 doped epoxy resin photopolymer. The mechanism of the photo-chemical reaction will be investigated and discussed. Finally, section 5 gives the conclusions of this paper.

2. Characteristics of holographic recording in PQ/PMMA photopolymer at 532 nm

In order to investigate the characteristics of the PQ/PMMA photopolymer for holographic recording at a wavelength of 532 nm, we have fabricated 2 mm thick samples using the previous two-step thermo-polymerization technique [29, 31]. A two-beam interference optical setup was applied for holographic recording. A plane wave at 532 nm was split into two beams with an intensity ratio at 1:1, and they were incident into the sample symmetrically with an intersection angle of 30° in air. The peristrophic multiplexing technique was applied to record 200 holograms in one location of the photopolymer. The exposure energy density for each hologram was 4.46 J cm^{-2} . The diffraction efficiencies (defined as the ratio of the intensity of the diffracted beam to that of the summation of the diffracted and the transmitted beams) of the recorded gratings were measured after recording. The summation of the square roots of the diffraction efficiencies forms a running curve of the cumulative grating strength, i.e. $C(E) = \sum_{i=1}^n \sqrt{\eta_i}$, where n is the total number of holograms that have been recorded for a total exposure energy density of $E \text{ J cm}^{-2}$. By curve fitting with the function: $C(E) = C_{\text{sat}}[1 - \exp(-E/E_\tau)]$, the saturation value C_{sat} of the curve gives the dynamic range of the material, $M\#$ and E_τ give the exposure energy constant of the material. The material sensitivity, S , is defined to be an increment in the cumulative grating strength with respect to the amount of exposure energy. When the sample is unexposed, $S = dC/dE|_{E \rightarrow 0}$. According to the running curve function, the sensitivity can be found to be: $S = C_{\text{sat}}/E_\tau = M\#/E_\tau$. The $M\#$ and S indicate the capability of that material for volume data storage.

Figure 1 shows the experimental results. It can be estimated from the figure that the $M\#$ and S at 532 nm are 1.7 and $0.009 \text{ cm}^2 \text{ J}^{-1}$, respectively. These characteristics are far below what are required to achieve holographic data storage disks for TB capacity and Gb s^{-1} data rate. Low sensitivity is especially a more serious problem when operating at 532 nm. For a comparison, the experimental result at 514 nm is also shown in figure 1. It is seen that the $M\#$ and S at 514 nm are 3.3 and $0.69 \text{ cm}^2 \text{ J}^{-1}$, respectively. The $M\#$ at 532 nm is about half and the sensitivity is about two orders of magnitude lower than that at 514 nm. The reason for such a huge degradation could be attributed to the fact that the resonance frequency of the PQ molecule is far away from 532 nm. According to our investigations, the physical mechanism of holographic recording in our PQ/PMMA is attributed to the photo-induced radical generation and the resulting chemical attachment with MMA, and this structural change of the PQ molecule produces a refractive index change to form the phase grating. Thus, if the light wavelength is away from the resonance frequency range of the photosensitive molecule, in this case PQ molecules, the hologram recording characteristics will be reduced. Figure 2

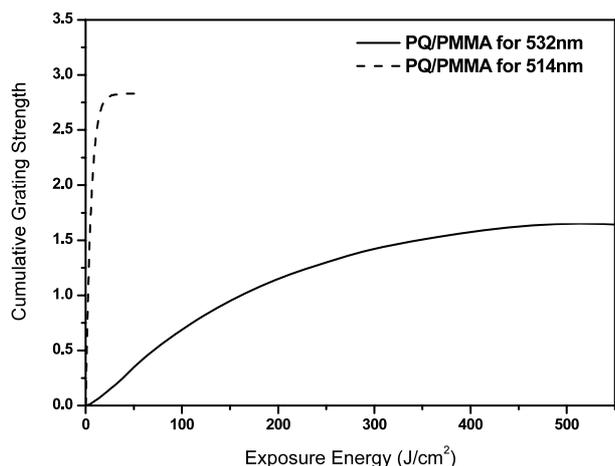


Figure 1. The running curves of multiple-hologram recording in PQ/PMMA samples: dashed line for 514 nm and solid line for 532 nm.

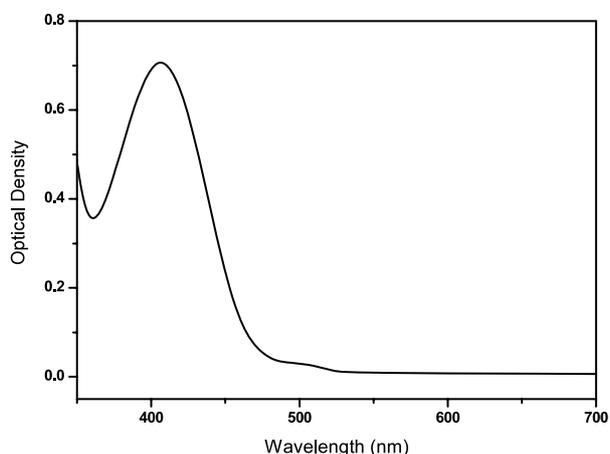


Figure 2. The typical absorption spectrum of PQ molecules in MMA solvent.

shows the absorption spectrum of PQ molecules dissolved in MMA solvent [32]. It can be seen that 532 nm is almost at the long tail of the peak spectral response of the radical generation, thus, the efficiency for optical recording is greatly reduced.

A straightforward way to improve this material at 532 nm is simply to replace PQ with a new photosensitive molecule which has a resonance frequency close to 532 nm. Irgacure molecules, one class of titanocene photo-sensitizers, are possible choices. They are usually used for initiating the photopolymerization of acrylate monomer materials with green light [33]. The absorption spectra of one class of these photosensitive elements, named Irgacure 784, dissolved in MMA solvent is shown in figure 3. It can be seen that the absorption coefficient is larger than that of PQ molecules at 532 nm shown in figure 2.

Further, figure 4 shows the molecular structure and photo-dissociation of Irgacure 784 [33]. As is illustrated, under light exposure the four chemical bonds between titanium atom

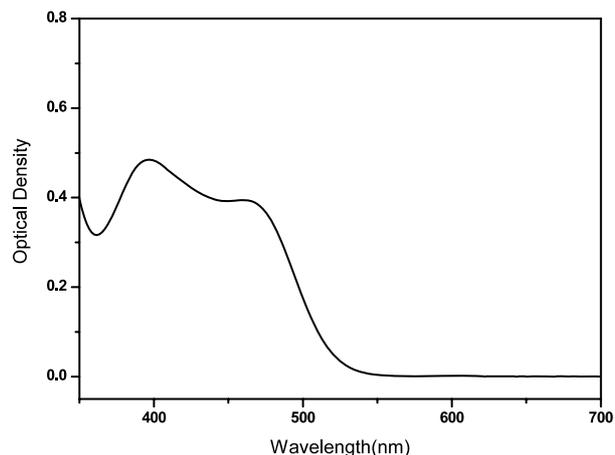


Figure 3. The typical absorption spectra of Irgacure 784 molecules in MMA solvent.

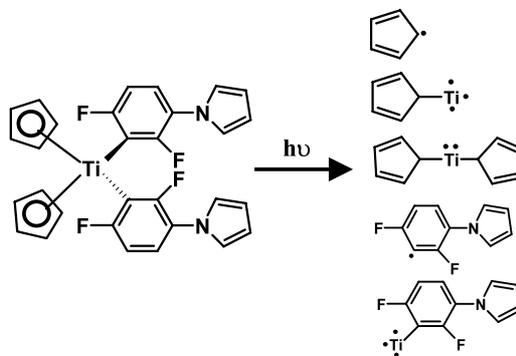


Figure 4. The molecular structure and photo-dissociation of the Irgacure 784 molecule.

and other two ligands, η^5 -2,4-cyclopentadien-1-yl and 2,6-difluoro-3(1H-pyrrol-1-yl)phenyl may be broken into several intermediate radicals. These radicals can either recombine to form a new photoproduct [34] or initiate polymerization of the monomers, which is similar to the chemical property of the photoexcited PQ radical. This indicates the possibility of the photo-induced chemical reaction of Irgacure 784 molecule with MMA, of which a new photoproduct with less conjugated structure will be formed and a corresponding phase grating will be produced. Hence, replacing PQ by Irgacure 784 in PMMA should be able to improve the holographic recording at 532 nm. In order to fabricate a material with a strong polymer matrix such that the photo-induced shrinkage effect is negligible, we applied the two-step thermo-polymerization technique in fabricating Irgacure 784 doped PMMA.

3. Irgacure 784 doped PMMA photopolymer

3.1. Sample fabrication

Irgacure 784 with 0.0034 mol% (namely, 1.79 wt%) was first added into the liquid MMA monomer. Notice this molar

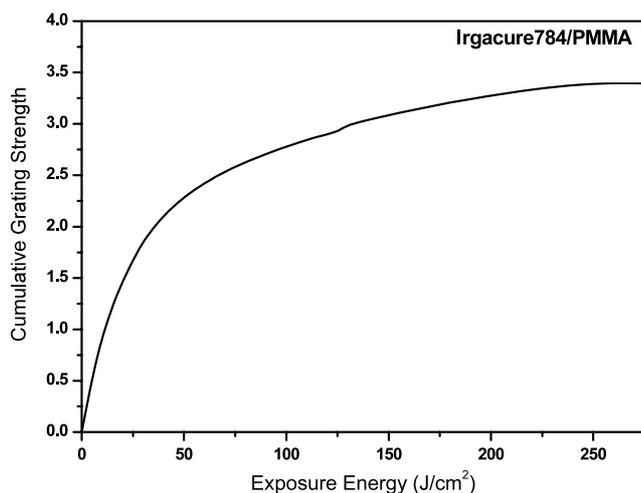


Figure 5. The running curve for the cumulative grating strength in Irgacure 784/PMMA sample.

concentration was the same as that of the PQ in PQ/PMMA, so that a comparison of holographic characteristics can be made between the two photopolymers. Then, thermo-initiator, 2,2-azo-bis-isobutyronitrile (AIBN) with a concentration of 1 wt% was added into the solution, and the solution was stirred at 30 °C for 4 h until all components were dissolved completely. The solution was then percolated using a syringe filter with a hole size of 0.2 μm . After this preparation, the percolated solution was ready for the two-step thermo-polymerization process. In the first step, the solution was stirred at 30 °C for around 24 h until the solution became homogeneously viscous. In the second step, the sticky solution was poured into a glass cell with dimensions of 10 cm \times 10 cm \times 2 mm for molding, and the whole set was baked at 45 °C for 3 days until most of the MMA monomers were polymerized to form a solid polymer bulk. This completed the fabrication procedures.

3.2. Characteristics for volume holographic data storage

Holographic data storage characteristics were examined by recording 200 plane-wave holograms at one location of the material with 532 nm laser beams. In the experiment, each hologram was recorded with an exposure energy of 1.69 J cm⁻². The running curve for the cumulative grating strength is shown in figure 5. Comparing the running curve with that for PQ/PMMA in figure 1, it can be seen that the Irgacure 784/PMMA sample possesses a much faster response.

Following the procedures of curve fitting of figure 5, the parameters $M\#$ and E_τ were obtained, and the sensitivity S was then calculated. It was found that the sensitivity of this sample had increased significantly to $7.6 \times 10^{-2} \text{ cm}^2 \text{ J}^{-1}$, which is about 10 times larger than that of the PQ/PMMA sample ($9 \times 10^{-3} \text{ cm}^2 \text{ J}^{-1}$) at wavelength 532 nm. On the other hand, the $M\#$ of Irgacure 784/PMMA sample was 3.26, which is about two times that of PQ/PMMA ($M\# = 1.7$).

These results show that holographic characteristics of Irgacure 784/PMMA have been improved. Replacing PQ with Irgacure 784 indeed provides a better spectral response at

532 nm. With the sensitivity $7.6 \times 10^{-2} \text{ cm}^2 \text{ J}^{-1}$, the material is able to support a higher data recording rate than that of PQ/PMMA at 532 nm. However, it is still far away from our goal of $35 \text{ cm}^2 \text{ J}^{-1}$ to achieve a Gb s⁻¹ holographic disk. In the next section, we describe how to modify the doped elements for further improvement of the holographic characteristic of doped photopolymer.

3.3. Analyses on photo-chemical reaction

We first examined the photo-induced chemical reactions in Irgacure 784/PMMA. The sample was first illuminated by a 532 nm DPSS laser beam with an exposed energy density of 250 J cm⁻². Then, the mass spectrum was measured with a TRIO-2000 from VG Biotech Co. It provides information about the molecular weight distribution of the compounds in the material. Figure 6 gives the experimental results. Several important peak signals appear and can be useful to illustrate the photo-chemical reaction of Irgacure 784 and MMA. They are labeled with the large numbers and the corresponding chemical structure, as shown in figure 6. Three points are to be noticed, first, the two peak signals at molecular weights of 113 and 178 represent the radicals of ligand, η^5 -2,4-cyclopentadien-1-yl, bonding to titanium atoms, respectively. They are the intermediate radicals produced by light exposure, as shown in figure 4. Second, the peak signal at a molecular weight of 179 represents the existence of 2,6-difluoro-3(1H-pyrrol-1-yl)phenyl. The peak signal at a molecular weight of 243 represents the existence of (η^5 -2,4-cyclopentadien-1-yl)-[2,6-difluoro-3(1H-pyrrol-1-yl)phenyl]. These two compounds are two of the final photoproducts of Irgacure 784. They indicate the possibility of the recombination of the intermediate radicals. Third, another characteristic signal appears at 343 by molecular weight. Since the molecular weights of (η^5 -2,4-cyclopentadien-1-yl)-[2,6-difluoro-3(1H-pyrrol-1-yl)phenyl] and MMA are 243 and 100, respectively, the appearance of peak signal at 343 gives evidence that the largest photoproduct in Irgacure 784/PMMA sample could be the mixture of one Irgacure 784 broken fragment attached to one residual MMA molecule.

The mass spectrum measurements show that Irgacure 784/PMMA photopolymer fabricated by our two-step thermo-polymerization technique follows a similar recording mechanism to that of the PQ/PMMA photopolymer [30]. Therefore, we anticipate this sample to also possess a characteristic of minimal photo-induced shrinkage, which is crucial for volume holographic recording. This has been confirmed by our holographic experiments, because all the 200 recorded gratings have been well reconstructed. The results also indicate that, if we could increase the radical and monomer concentrations in the polymer matrix, it may be possible to increase the photo-chemical reaction rate so as to improve the holographic recording characteristics.

3.4. Improvement of the Irgacure 784/PMMA

The above results show that the two-step thermo-polymerization technique is able to produce a polymer material with a strong

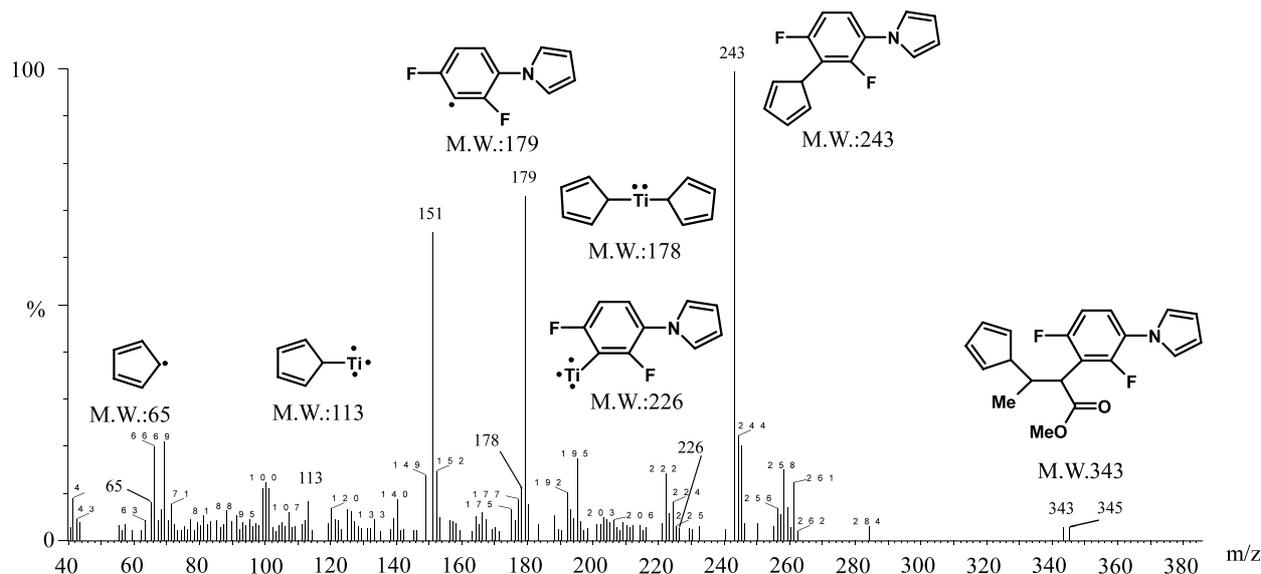


Figure 6. The mass spectrum of the Irgacure 784/PMMA sample after an optical exposure.

matrix so that the photo-induced shrinkage is negligible. However, the holographic characteristics are restricted. The reasons for that could be understood from our previous investigation on the fabrication procedures and recording mechanisms. During the fabrication stage, most of the monomers have been transformed into a polymer matrix, only a small amount (~ 2 wt%) were left for holographic recording. In addition, the solubility of photosensitive elements such as PQ in MMA solvent is limited (~ 0.7 wt%). As a result, the total concentration of doped elements available for holographic recording in our doped photopolymer system is so low that $M\#$ and S are restricted.

Based on this information, two strategies could be taken to improve the situation. Firstly, instead of PMMA, we find other components to form a strong polymer matrix during the fabrication procedure. This matrix should be able to stay unaffected by the holographic recording procedure. Secondly, instead of relying on the residual monomers, we dope other elements into the polymer matrix to perform the photo-chemical reaction for holographic recording. The concentrations of these elements should be able to adjust and increase independent of the other components for forming the photopolymer. In this way, a high sensitivity holographic recording material with minimal shrinkage could be designed.

The key here is to find suitable components that are adapted to our two-step thermo-polymerization fabrication technique. For the first part, we choose cationic epoxy components to be responsible for forming polymer matrix through the thermo-polymerization procedures. For the second part, we choose appropriate monomers to incorporate with Irgacure 784 to form the photo-chemical components responsible for holographic recording. These two parts will take place through different mechanisms: polymer matrix formation through thermo-induced cationic epoxy resin polymerization, and holographic recording through photo-induced chemical reactions. The mutual influence between them should be small so that the two parts can be adjusted independently of each other. This material can be considered

as an epoxy resin photopolymer doped with Irgacure 784 plus monomers, and we named it Irgacure 784 doped epoxy resin.

4. Irgacure 784 doped epoxy resin photopolymer

4.1. Sample fabrication

As described in the previous paragraph, the material system consists of two parts, the epoxy resin polymer matrix and the doped photosensitive elements. Two components are chosen for the polymer matrix: bisphenol A diglycidyl ether (BADGE) and *N*-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane (3APTS). Four components are chosen for the doping elements: monomers 2-hydroxyethyl methacrylate (HEMA) and acrylamide (AA), photosensitive Irgacure 784 and diphenyliodonium iodide (DI). Figure 7 shows the chemical structures of all components.

In the fabrication procedures, solutions of the two parts, the matrix solution and the doping elements solution were prepared separately. The matrix solution was prepared by mixing BADE and 3APTS with a molar ratio of 3:2, stirring at 25 °C for 30 min. The doping elements solution was prepared by dissolving 30 wt% of AA, 1 wt% of Irgacure 784, and 0.01 wt% of DI into HEMA solvent. The solution was percolated through a syringe filter with hole size of 0.2 μm . Then, in the first step, the two solutions with a weight ratio of 7:3 were mixed together and stirred at 25 °C for 30 min before being poured into a glass cell and baked in an oven at 45 °C for another 12 h. In the second step, the oven temperature was increased to 100 °C and retained for another 1 h until the solid sample was obtained. Through these procedures, BADE and 3APTS were polymerized to form an epoxy resin matrix through cationic polymerization. At the same time, the doping elements, HEMA, AA, Irgacure 784, and DI were dispersed uniformly in the epoxy matrix. The samples were fabricated into 2 mm thick slabs with good optical quality by visual inspection.

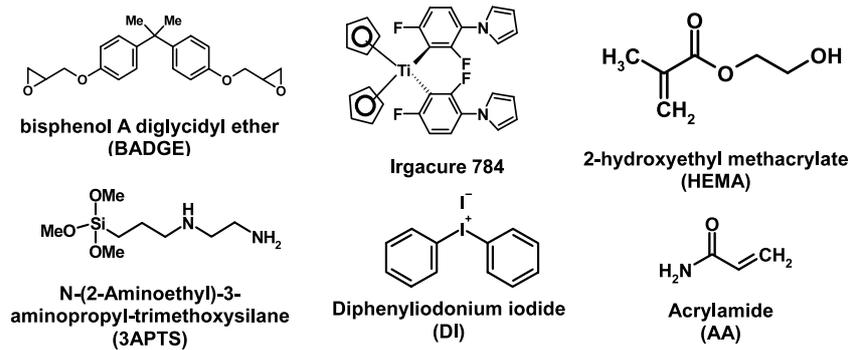


Figure 7. The chemical structures of all compounds for Irgacure 784 doped epoxy resin photopolymer.

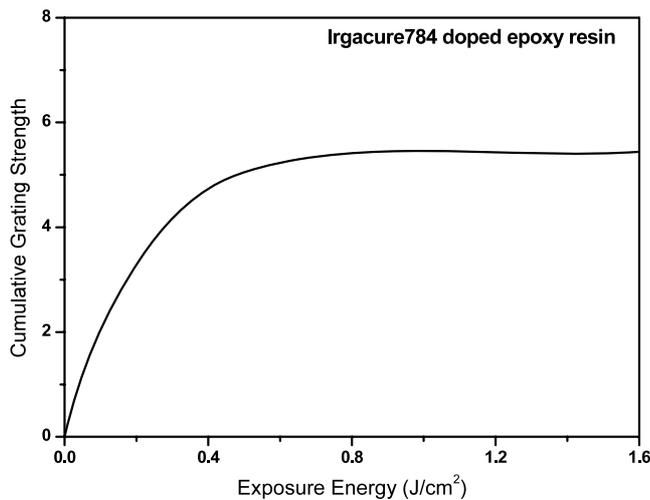


Figure 8. The running curve for the cumulative grating strength in Irgacure 784 doped epoxy resin photopolymer.

4.2. Characteristics for volume holographic data storage

In experiments, 190 plane-wave holograms were recorded at one location of the sample, of which each hologram was recorded with an energy density of 176 mJ cm^{-2} from a 532 nm laser source. After holographic recording, all the recorded gratings in this 2 mm thick sample were read out completely by using the original reference plane wave. It indicates that the Bragg condition for all volume gratings has been matched well, and that photo-induced shrinkage in this material is low enough to support multiplexed holographic recording in the volume. The diffraction efficiencies of the volume gratings were measured and the running curve for the cumulative grating strength was obtained, as shown in figure 8. Comparing this curve with the result for Irgacure 784/PMMA in figure 6, it is obvious that the Irgacure 784 doped epoxy resin photopolymer possesses a dramatic improvement in both $M\#$ and S .

The parameters $M\#$ and sensitivity S of the material were calculated from an exponential function fitting of the running curve. It is found that the $M\#$ and S of the Irgacure 784 doped epoxy resin are 5.49 and $26.65 \text{ cm}^2 \text{ J}^{-1}$, respectively. The $M\#$ is around 1.7 times larger, whereas the sensitivity is about 350 times higher than that of Irgacure 784/PMMA

sample. According to the system evaluation of holographic data storage, with a 100 mW DPSS laser, this material will be able to support a data recording rate of 760 Mb s^{-1} . This is very close to our requirement for supporting Gb s^{-1} holographic disks.

4.3. Analyses on photo-chemical reaction

In order to investigate the photo-chemical reaction in our sample and so understand the physical mechanism of holographic recording, we have performed solid state $^1\text{H-NMR}$ spectrum measurements and thermogravimetry analyses (TGA) of the samples at two different states: unexposed and exposed. The unexposed state means the sample was as prepared. The exposed state means the sample was illuminated by a 532 nm DPSS laser beam until it became colorless.

$^1\text{H-NMR}$ spectrum measurement is usually used to analyze the organic compound structure by inspecting the chemical shift of hydrogen atoms with respect to the common standard TMS, tetramethylsilane [35]. By measuring the solid state $^1\text{H-NMR}$ spectrum of the two states, one can identify the photoproducts induced by optical exposure. The measurements were performed by using a DSX400WB from BRUKER Co. Figure 9 shows the experimental results. It can be seen that broadband signals appear from -10 to 10 ppm in both states of the sample. The signals are broadband because they come simultaneously from the epoxy-resin matrix and the doped elements, which are mixed together. However, several characteristic peaks can still be seen clearly, which provide us with a possibility to identify the organic components in these samples.

For both material states, peak signals appear at around 1.5 and 3.3 ppm. These are produced by the hydrogen atoms in the alkanol-OH and *N*-methyl functional groups, respectively. Both these two functional groups can be found in the chemical formula of the epoxy-resin matrix, as well as those of AA and HEMA monomers. Thus, from $^1\text{H-NMR}$ spectrum measurements it can be proposed that the polymer matrix of our sample is formed by cationic polymerization of BADE and 3APTS, within which AA and HEMA monomers were successfully doped.

Further comparison between the two spectra reveals that peak signals at around 4.42 and 5.09 ppm are missing in the after exposure sample. These signals represent hydrogen

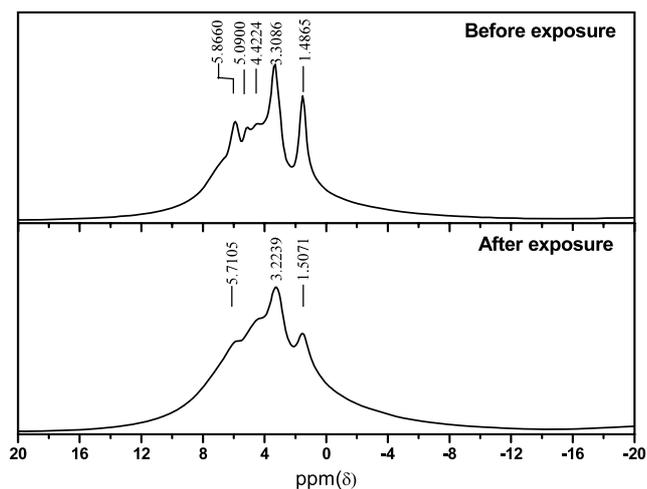


Figure 9. The solid state $^1\text{H-NMR}$ spectra of the Irgacure 784 doped epoxy-resin sample before and after light exposure.

atoms in the alkene-CH functional groups of HEMA and AA. Disappearance of these signals indicates that under light illumination the vinyl groups in the monomers have been reacted by Irgacure 784 radicals to carry out polymerization. In other words, photo-induced polymerization of the doped elements is a possible mechanism for holographic recording in Irgacure 784 doped epoxy resin photopolymer.

To further confirm the material components of our photopolymer, TGA measurements of the samples were performed by a TA Q500 from DuPont Co. Figure 10 shows the experimental results for the samples before and after optical exposure, which are denoted by the solid and dashed lines, respectively. The derivatives of weight loss curves, plotted as a function of temperature, are also shown in the figure. For both states of the samples, it can be observed that there is a two-stage weight loss when the sample was heated from low to high temperatures. The weight loss in the low temperature regime ($<330^\circ\text{C}$) can be attributed to degradation of small molecules including monomers, photo-sensitizers and even photoproducts. The weight loss of the sample in the higher temperature regime ($>330^\circ\text{C}$) can be considered as a degradation of the epoxy matrix. This two-stage structure of the weight loss in TGA measurements indicates that this material can be considered as consisting of two groups of components, one, the strong polymer matrix, and two, doping elements and their compounds. This result confirms that our two-step thermo-polymerization technique can fabricate a holographic recording material which consists of a strong polymer matrix and doped photosensitive elements. This characteristic facilitates the material to be able to record multiplexed volume gratings with minimal photo-induced shrinkage effect.

The difference in the derivatives of the weight loss of the two states reveals some further information about the mechanisms of holographic recording. For the unexposed sample, as illustrated by the solid line, two broad peaks appear in the regimes from around 100 to 150°C and from 225 to 275°C , respectively. These two signals can be considered as

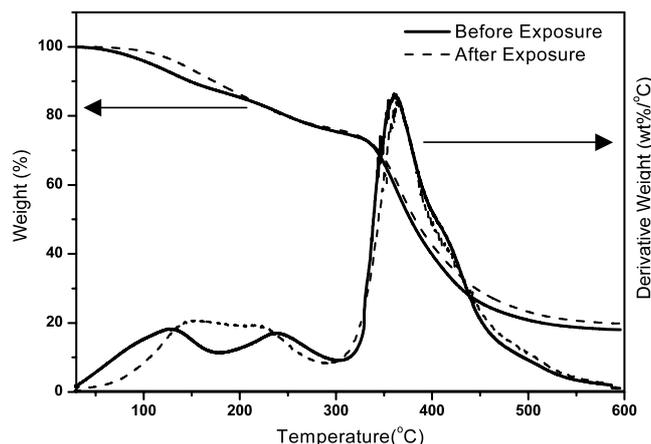


Figure 10. The thermogravimetry analyses of Irgacure 784 doped epoxy-resin sample before and after light exposure.

thermal degradation of the monomers and photo-sensitizers, which occur at different temperatures. It is interesting, as illustrated by the dashed line, that after exposure these two regimes merge together to become a broadband signal in the regime from 120 to 250°C . This signal is considered to result from thermal degradation of the photoproducts, whose breaking temperature is higher than the MMA and HEMA monomers. These photoproducts can be attributed to be either oligomers or polymers with short chains formed by the polymerization of HEMA and AA monomers excited by the photo-sensitizers, Irgacure 784, under light exposure.

In both states, we observe strong broadband signals at above 300°C . It can be considered as thermal degradation of the epoxy resin. Note that the two states appear to be almost identical in the high temperature regime. This implies that optical exposure does not have any effect on the polymer matrix. As a result, we can conclude that the physical mechanism of the holographic recording in Irgacure 784 doped epoxy resin photopolymer is mainly related to the photo-induced short-chain polymerization of doping elements.

5. Conclusion

We have fabricated Irgacure 784 doped PMMA photopolymers and Irgacure 784 doped epoxy resin photopolymers for volume holographic data storage at 532 nm . The design strategy and fabrication technique have been described, and the holographic characteristics of the materials have been characterized. Comparing the experimental results of Irgacure 784/PMMA to those of PQ/PMMA, the $M\#$ has been improved by about 1.9 times and the sensitivity has been improved by ~ 10 times. These experimental results reveal that Irgacure 784 molecules are efficient in shifting the holographic recording sensitivity to the wavelength at 532 nm . By adding AA and HEMA monomers, together with photosensitive DI and Irgacure 784 to form the doping solution, and adding BADGE and 3ABTS together to form a polymer matrix solution, we have fabricated Irgacure 784 doped epoxy resin photopolymer through a two-step thermo-polymerization technique. The $M\#$ has been further improved by 1.7 times, and the sensitivity has been

improved by more than 350 times. According to our system evaluation method, this material is capable of supporting a holographic data storage system with a data recording rate of 760 Mb s^{-1} , which is very close to the ultra-high data storage at recording rate of Gb s^{-1} . These results suggest that epoxy-resin matrix-based photopolymer system provides an effective way to improve the holographic recording characteristics for volume data storage. We have performed $^1\text{H-NMR}$ and TGA analyses on the fabricated samples. The results indicate that the physical recording mechanism in this photopolymer follows our design strategy for producing holographic materials with a minimal shrinkage effect. Further improvement of the material can be achieved by optimizing the material components and the fabricating procedure.

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