

Holographic characteristics of organo-metallic compound doped PQ: PMMA photopolymers

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ABSTRACT

Photopolymers have been applied widely in optical devices for communications, displays, bio-sensing, and data storage. The advantages of this material are easy to synthesize, high refractive index change, high sensitivity and good optical quality. Recently, we have investigated on the syntheses and analysis of 9,10-PhenanthreneQuinone doped Poly(Methyl MethAcrylate) (PQ:PMMA) photopolymer. This material can be fabricated with large dimensions and with thickness in the range of several-centimeters. Experiments show that the material shrinkage is negligible after optical exposure such that our doped photopolymer is attractive for volume holographic applications. However, comparing with other photopolymers, our PQ:PMMA material has a drawback of lower sensitivity (~ 10 mW/cm²). In this presentation, we demonstrate that by adding organo-metallic compound (Zinc MethylAcrylate, ZnMA) into the PQ:PMMA photopolymer, we succeeded in reducing response time and increasing holographic diffraction efficiency of the material. We report the fabrication and experimental investigation of dye-doped photopolymer, and discuss their application for data storage.

Keywords: photopolymer, PMMA, volume hologram, organo-metallic molecule.

1. INTRODUCTION

Recently, volume holography has been investigated intensely. One of the research interests is in holographic data storage due to its attractive characteristics such as large capacity and fast data transfer rate. There are many important issues in developing holographic data storage including test bed, system integration, and recording materials. Among these, material is the key for the development of high quality data storage. There are many important material characteristics, such as dynamic range, high optical quality, photosensitivity, dimensional stability, low scattering and so on. Several kinds of materials have been developed, such as LiNbO₃, BaTiO₃, photorefractive polymer, etc¹. Roughly, it can be divided into inorganic and organic materials. Organic material, such as photopolymer is attractive because it has many advantages, including large refractive index modulation, low cost, easy fabrication, easy modified characteristics and so on. On the other hand, photopolymer still has some disadvantages such as dimensional shrinkage effect, material uniformity and reliability. Shrinkage effect is the most important one for volume holograms. If the Bragg condition is miss-matched then the recorded information will not be retrieved completely. The shrinkage effect limits the thickness of the conventional photopolymer materials to be hundreds μm to a few mm. We have fabricated and shown that PQ/PMMA photopolymer could be a potential material in holographic data storage²⁻⁵, because it has small shrinkage effect (shrinkage coefficient $< 10^{-5}$)^{6,7} and optical quality. It is easy to modify the parameters (both the compositions and the environmental conditions) to fabricate samples, which are several centimeters thick and have good dimensional stability. But there are still many improvements to be made in PQ/PMMA, including photosensitivity and refractive index modulation. One possibility to improve the sensitivity is to add another dye into PMMA polymer matrix. This extra-element can serve as a catalyst to accelerate the attachment of the PQ with MMA molecules, which induces large refractive index change in our photopolymer. Therefore, the material can still remain small shrinkage effect. It is known that under light illumination, organometallic compounds can react with the carbonyl group on the PQ to form new

compounds through addition reaction⁸. The response speed is usually faster than the direct photo-excitation of PQ molecule. We then choose Zinc MethylAcrylate (ZnMA) molecule as the extra dopant in our sample. In this paper, we present investigations on material fabrication and testing. We fabricate the samples that doped with different concentrations, and test their optical and holographic characteristics. By studying the characteristics of samples with different composition ratios between ZnMA and PQ, we analyze the role of each component for holographic recording.

2. MATERIAL FABRICATIONS

2.1 Components of the material

The monomer, Methyl methacrylate (MMA, 98% assay), was purchased from Lancaster Chemical Co. We distilled MMA by a vaporizing approach under suitable pressure and temperature conditions so as to remove the stabilizer from the material. When the vapor flow of MMA passes through the cooling tube, it starts to cool down and turn to the liquid phase. The purified MMA is obtained. The thermal initiator, 2,2-Azo-bis-isobutyronitrile (AIBN, 98%), was bought from Showa Chemical Co. It was purified in ethanol by a recrystallization approach. The chemical dye molecule 9,10-Phenanthrenequinone (PQ), was purchased from TCI Chemical Co. It was used as received. Zinc MethylAcrylate (ZnMA), Poly (methyl methacrylate) powder (PMMA, with average molecular weight of 120,000), and DiMethyl Formal amide (DMF), were bought from Aldrich Co. Figure 1 shows the molecular structure of all these compounds.

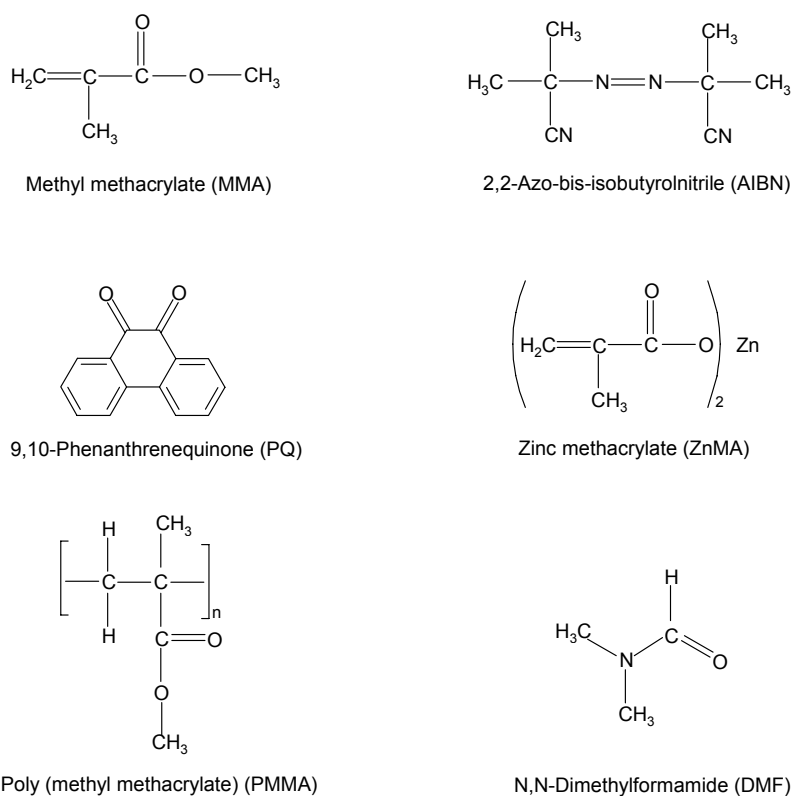


Fig. 1 The structures of compounds.

2.2 Photopolymer Preparations

In order to analyze the optical and holographic properties of our materials, we have made three kinds of doped photopolymers. Firstly, the thin film samples with thickness of ~hundred μm are made because they were easy to fabricate and maintain high optical quality. Therefore, the thin film samples are made to measure both optical and holographic characteristics. When we observe the improvement of these novel samples, we then make block samples with similar compositions for volume holographic recording. Secondly, we make 2-mm thick block samples. The PQ/PMMA sample is made for comparison with the novel ZnMA/PQ/PMMA samples. The notations of samples with different dopant concentrations for both thin film and block types are listed in Table 1. In this section, we describe the fabrications of these three samples.

2.2.1 ZnMA/PQ/PMMA

The thin films samples were made by the doctor-blade method. Firstly, we dissolved the PQ and ZnMA powders into DMF solvent and stirred the solution until it was dissolved completely. We then added the PMMA powder with concentration of 20% weight, stirred the solution at high temperature ($\sim 80^\circ\text{C}$) around 1 hr until the powder was dissolved. The solution was cooled down to room temperature. A doctor is then used blade to cast the polymer solution with thickness of 600 μm on the flat glass, and the samples are put in a vacuumed oven at 70°C for 3 days to dry the solvent DMF away and the solid photopolymer films were obtained. Fig. 2(a) shows the fabrication procedures for the thin films. The average thickness of the films was measured to be 100 μm . The samples of ZnMA and PQ doped PMMA polymer films are called as ZnMA/PQ in this paper. We have prepared samples with different weight percentages of PQ and ZnMA molecules.

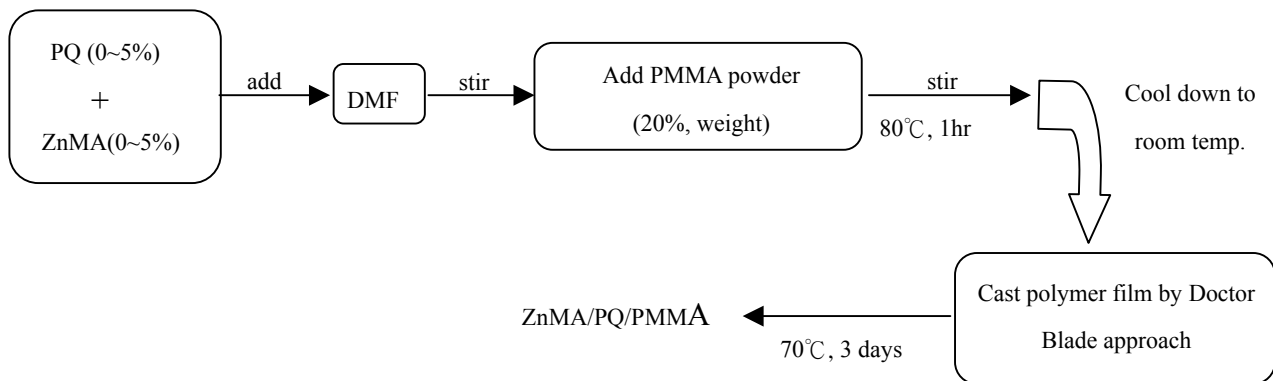


Fig. 2(a) Fabrication procedure of ZnMA/PQ/PMMA thin film photopolymer sample

2.2.2 PQ/PMMA blocks (by thermal polymerization)

PQ and AIBN (2% weight concentration) were added into MMA. The concentration of PQ was fixed at 0.7% weight, which is the saturated concentration for dissolution. The solution was stirred for 24 hours at constant temperature 30°C until the solution was dispersed and mixed very well. We then used a filter with the hole size of 0.2 μm to filter out impurities from the solution. The filtered solution was then used to make samples. In the first stage, it was stirred at 30°C for around 60 hrs until the solution is turned to high viscous. In the second stage the solution was poured into a glass cell and baked at 40°C for 3 days. Most of MMA molecules were polymerized in this procedure. This two-step procedure was found to obtain bulk photopolymer samples with good optical quality. The thicknesses of the samples were set at 2mm. In fact, depending on the temperature for polymerization, the concentration of the residual monomer MMA can be varied. In our samples, it was analyzed to be around 10 %.

2.2.3 ZnMA/PQ/PMMA blocks (by thermal polymerization)

A similar procedure (like PQ/PMMA) was used to fabricate ZnMA/PQ/PMMA samples. Firstly, ZnMA (0.07% weight and 0.175% weight) was added into the MMA and put into an ultrasonic bath, and then it was stirred until ZnMA dissolved well in MMA. The compound solution was stirred for about 1 hour. We then added PQ and AIBN into the ZnMA/MMA solution with PQ concentration at 0.7% weight and the AIBN concentration at 2%. The flow chart for

fabricating PQ/PMMA and ZnMA/PQ/PMMA photopolymers are described in Fig. 2(b). Our samples appear to be yellowish color, with a clear optical transmission. After the measurements of absorption and transmission spectra, we found it suitable to use argon laser with the wavelength 514nm as holographic recording light source.

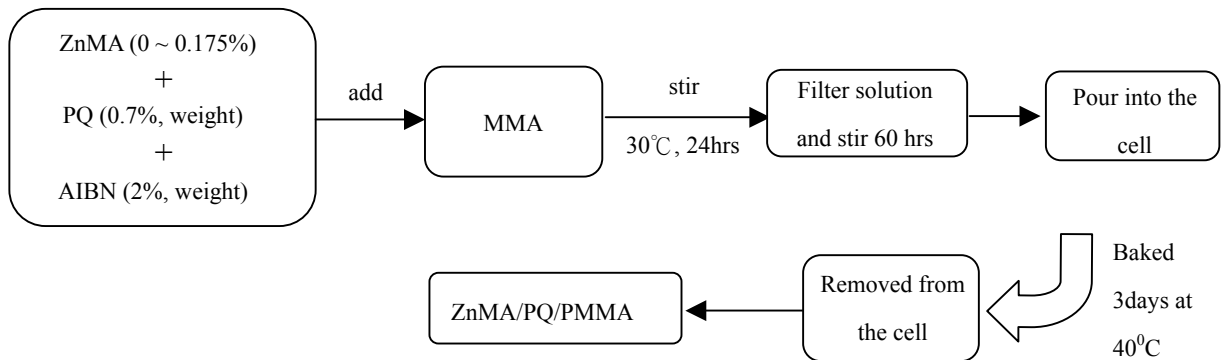


Fig. 2(b) Fabrication procedure for PQ/PMMA and ZnMA/PQ/PMMA photopolymers

Sample (Percentage of compositions)	Thin films samples(100μm) (doctor-blade method)					Block samples (2mm) (Thermo-polymerization)		
	PQ5 %	PQ 5% ZnMA 0.5%	PQ 5 % ZnMA 5%	PQ 0.5% ZnMA 5%	ZnMA5%	PQ0.7%	PQ0.7% ZnMA 0.07%	PQ0.7% ZnMA0.175%
Notation	PQ5	PQ5/ ZnMA0.5	PQ5/ ZnMA5	ZnMA5/ PQ0.5	ZnMA5	PQ0.7	PQ0.7/ZnMA 0.07	PQ0.7/ZnMA 0.175

Table 1. Samples of different compositions

(The percentage is in weight percentage of each compound in the photopolymer)

3. OPTIC CONFIGURATIONS FOR MATERIAL AND CHARACTERIZATION

We have performed optical and holographic experiments. Figure 3(a) shows the setup to measure transmission spectra. An Ar+ laser at wavelength 514nm was used as the pump beam. An Oriel monochromator with Xe and QTH-lamps provided the probe beam, which scanned the spectral range from 400 nm ~ 750 nm. The transmission spectra were detected by a photo-multiplier tube (PMT). Photopolymer samples were measured in two states: before and after exposure. The former state (before exposure) means the sample was kept at dark after it was fabricated. In order to reach the exposed state, the fresh samples (before exposure) were illuminated by the pump beam at 514 nm with intensity ~ 110 mW/cm² for several minutes until the samples become transparent. Transmission spectra could provide the information about the sensitive spectral range of the sample. In addition, the difference of the transmission spectra

between the two states is called the light-induced absorption change of the sample, which can help us to recognize the roles of each component in photoreaction. Figure 3(a) can also be used to measure the dynamics of light-induced absorption (change of transmission as a function of illumination time) of the sample at a particular wavelength, with a pump beam illuminates the sample simultaneously. Usually, the probe beam is selected at the wavelength for the largest change in absorption. In our experiments, the probe beam was set at 632 nm and the pump beam at 514 nm. The dynamics of light-induced absorption of the sample will indicate the temporal response of photoreaction between components such as ZnMA and PQ.

Figure 3(b) shows the optical setup for holographic measurements, which is a typical nondegenerate four-wave mixing. A collimated light beam from an argon laser with wavelength of 514 nm and total intensity 110 mW/cm^2 was divided into two beams with equal intensity. They were incident onto the sample symmetrically with an intersection angle of 32 degrees 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 Coherent Innova 300 and the He-Ne laser was JDS 1144P. In addition, in order to measure the dynamic range of block sample for holographic recording, the sample was placed on a rotational stage to perform peristrophical multiplexing for recording multiple holograms.

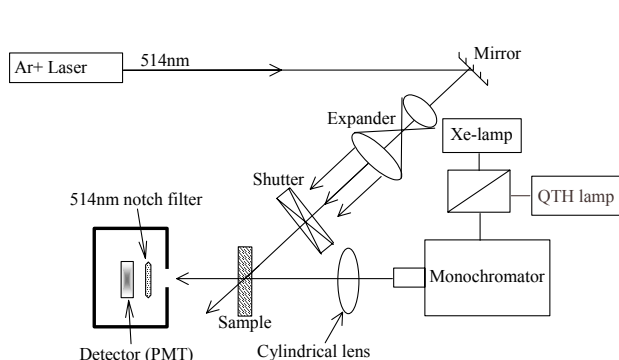


Fig. 3(a) Optical setup for transmission spectra and dynamic of light-induced absorption measurement

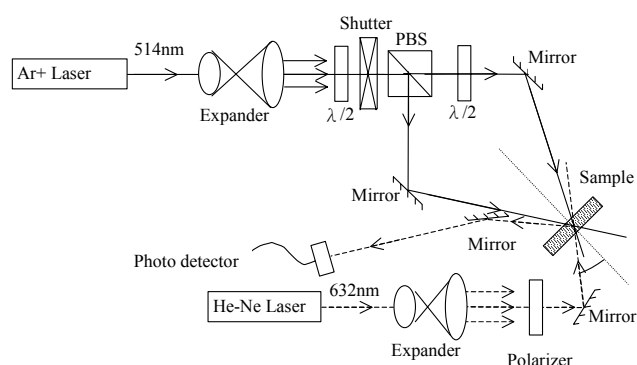


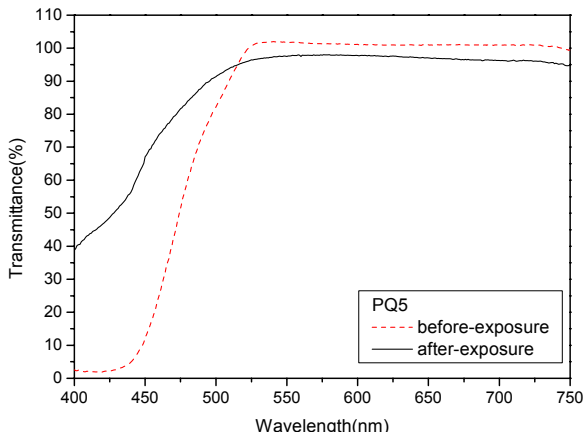
Fig. 3(b) Optical setup for holographic characteristics measurement

4. EXPERIMENTAL RESULTS

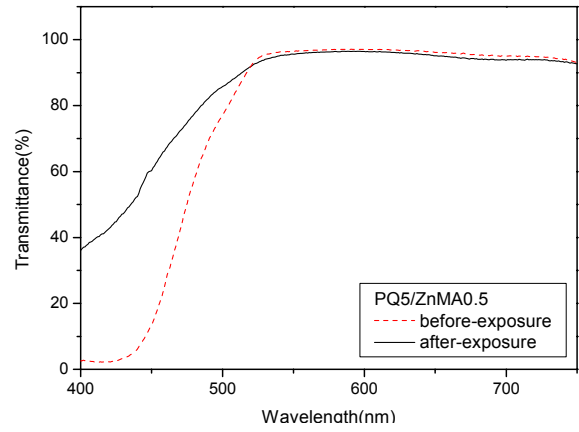
4.1 Transmission Spectra

Figure 4 is the transmission spectra of different samples with various concentration ratios between ZnMA and PQ. The dashed lines in the figures represent the before exposure state and the solid lines represent the after-exposure state, respectively. The effect of dopant ZnMA can be found by comparing the transmission spectra of Fig.4 (a), Fig.4 (b), and Fig.4 (c). When PQ concentration is fixed at 5% weight, the transmission spectra of before-exposure samples remain unchanged when concentration of ZnMA is increased from 0% to 5% weight. On the other hand, the after-exposure samples become more absorptive in long wavelength ranges (600 nm ~ 700 nm) and more transparent in short (< 500 nm). As the concentration of ZnMA increases, the absorption in the long wavelength regime changes abruptly from transparent to seriously absorptive. A strong absorption peak appears at ~ 680 nm for PQ5/ZnMA5 samples.

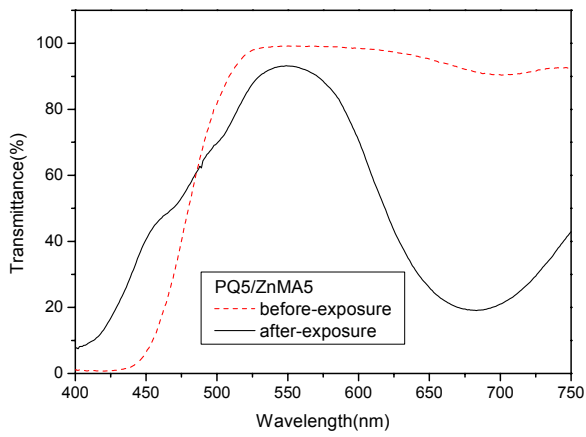
The effect of PQ concentration on the transmission spectra of the samples can be seen in Fig. 4(c), Fig. 4(d), and Fig.4 (e). In the before-exposure state, a large change of transmission spectra in short wavelength regime occurs when PQ concentration is decreased from 5 to 0%. The sample becomes more transparent in short wavelength regime as the concentration of PQ is reduced. Also, for the samples in the after-exposure state, when the concentration of ZnMA molecule is fixed at 5% weight and that of PQ molecule decreases from 5% to 0% weight, the samples become more transparent in both short wavelength (< 500nm) and long wavelength (> 600nm) regimes. In Fig. 4(e) with the pure ZnMA-doped PMMA sample, the transmission remains at 100% in the whole visible regime. This means that the samples with only doped ZnMA do not absorb light from 400nm to 750nm and therefore are not suitable for holographic recording in this spectral regime. In other words, PQ molecules are necessary if the material is to be used in this spectral regime.



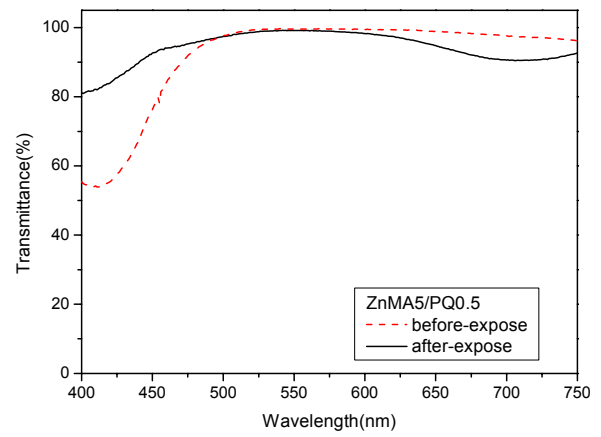
(a)



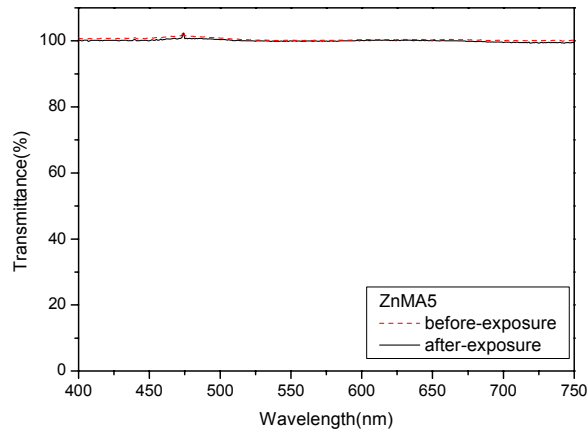
(b)



(c)



(d)



(e)

Fig.4 The transmission spectra of before- and after-exposure states. (a) PQ5, (b) PQ5/ZnMA0.5, (c) PQ5/ZnMA5, (d) ZnMA5/ PQ0.5, and (e) ZnMA5

From above analyses of light-induced changes of transmission spectra, we can summarize the possible photoreaction of photopolymer. It is known that organozinc compounds can react with the carbonyl group on the PQ to form new compounds through addition reaction.⁸ Though ZnMA molecule is not a photosensitive dye but it may serve as a catalyst, which provides an extra route for electron transfer to accelerate the excitation rate of PQ molecules. When a light with proper wavelength illuminates PQ molecules, PQ molecules will first combine with ZnMA and turn into the singlet-excited state, and then change to the triplet-excited state. Because of singlet-excited state transition is a rapid process, most photoreactions of PQ will proceed to the triplet-excited state. Then it will form a radical-ion pair by proton or H-atom transfer, which is derived from H-donor compounds.^{9,10} The PQ are easy to attach with the MMA monomer or the functional group on the PMMA polymer chain by 1,2 addition or H-subtraction to form final products. Therefore, during optical exposure PQ plays the role for the photosensitizer, and after light exposure, the structural change of the PQ molecule results in a refractive index change of the material. Thus it provides a mechanism for holographic recording.

4.2 Dynamics of light-induced transmittance

In order to further identify the role of ZnMA in photoreaction, we have measured the dynamics of light-induced transmittance of the samples, both in liquid and solid forms. The liquid solution was prepared by dissolving ZnMA and PQ molecules into a DMF solvent. The concentrations of both components were 1% weight. An argon laser at 514nm was used as the pump beam and a He-Ne laser with wavelength of 632 nm was used as the probe light to illuminate the solution. The transmitted intensity was measured as a function of time. Figure 5 shows the normalized transmittance. It can be seen that the transmittance first decreases very quickly and then gradually returns to high value. Because there is no PMMA molecule in the solution, thus the photoreaction between PQ and PMMA polymer can be negligible, and the quick decreasing in transmittance can be considered as the photoreaction between PQ and ZnMA molecules. These photoproducts are the intermediate state, which cannot stay for a long period. With further illumination, the photoproducts break to PQ radicals, which then follow chemical reactions to attach with other functional groups on ZnMA molecules. Therefore, the transmittance of the sample gradually recovers until it becomes fully transparent. We have also measure the dynamics of light-induced transmittance of the thin film samples. The results are shown in Fig. 6.

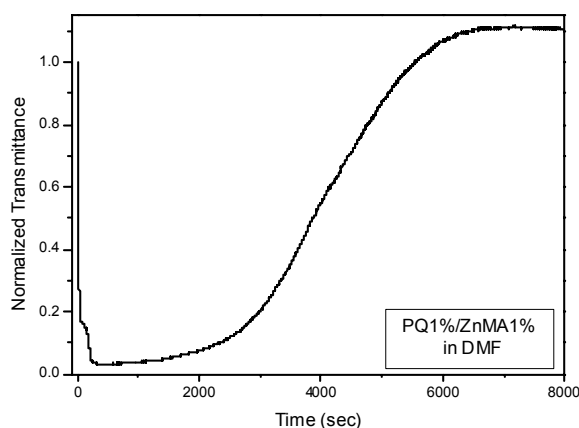
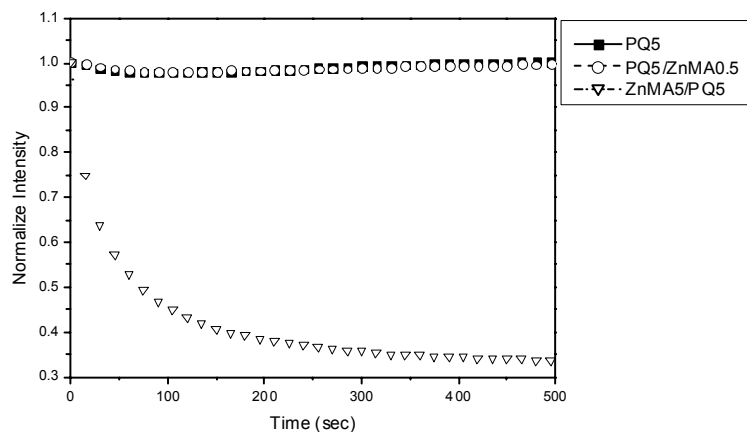
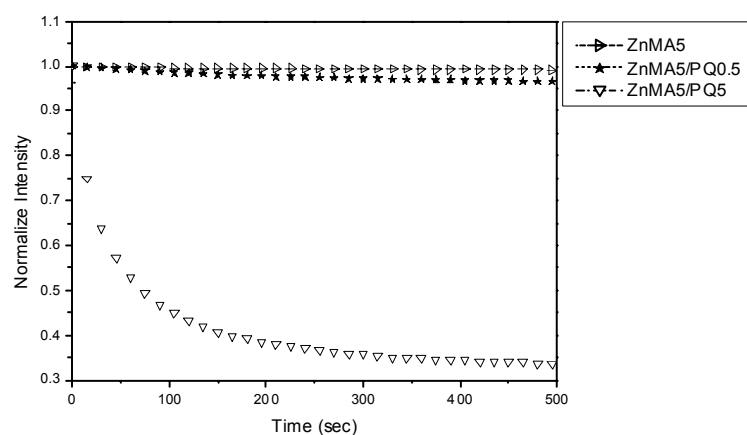


Fig. 5 Normalized dynamic transmittance of the solution, pump beam at 514nm and probe at 632nm.



(a)



(b)

Fig. 6 Normalized dynamic transmission change of the dry films, probe at 632nm and pump beam at 514nm.
 (a) PQ fixed and ZnMA varying and (b) PQ varying, and ZnMA fixed

Figure 6(a) shows that the dynamics of light-induced transmissions of pure PQ doped PMMA (marked by ■) drop slightly at the first 50 sec and then grows back slowly. The change range of the normalized transmittance is around 2% (from the lowest to the highest value). On the other hand, the behavior of PQ5/ZnMA5 (5% weight, marked by ▽) is very different. The transmittance shows an exponential decay which drops rapidly in 200 sec and then decreases further from 200 sec to 500 sec. This result implies that in order to introduce a significant change in photoreaction a certain amount of ZnMA should be doped.

The similar effect also can be observed when ZnMA concentration is fixed and PQ is increasing. It is seen in Fig. 6(b) that the transmittance of pure ZnMA doped PMMA (marked by ▷) and ZnMA5/PQ0.5 (0.5% weight, marked by ★) maintains in the range of 1 and 0.96. When the doped concentration of PQ is increased to 5% weight, the normalized intensity decreases from 1 to 0.34 by an exponential decay temporal form. Again, it shows that in order to introduce significant value of light-induced change in transmission, the concentration of PQ should be larger than a certain value. In order to estimate the effects of ZnMA and PQ dopants on the photoreaction, we have performed a curve fitting for Fig. 6(b) by the exponential function, shown below

$$I = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2}$$

where I represents the normalized intensity of the transmitted light, t represents the illumination time, and τ_1 and τ_2

represent the characteristic time constants, respectively. The results are summarized in Table 2.

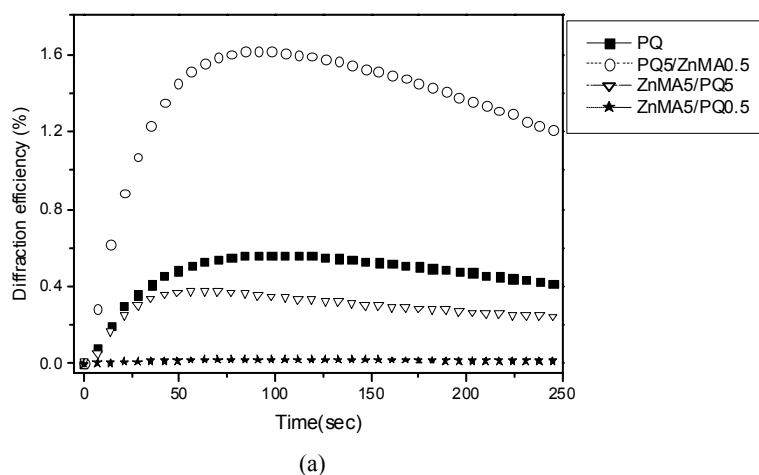
Sample	ZnMA = 5 % weight	
	ZnMA5 / PQ0.5	ZnMA5 / PQ5
Time Constant (sec)	$\tau_1 = 98$ $\tau_2 = 447$	$\tau_1 = 25$ $\tau_2 = 145$

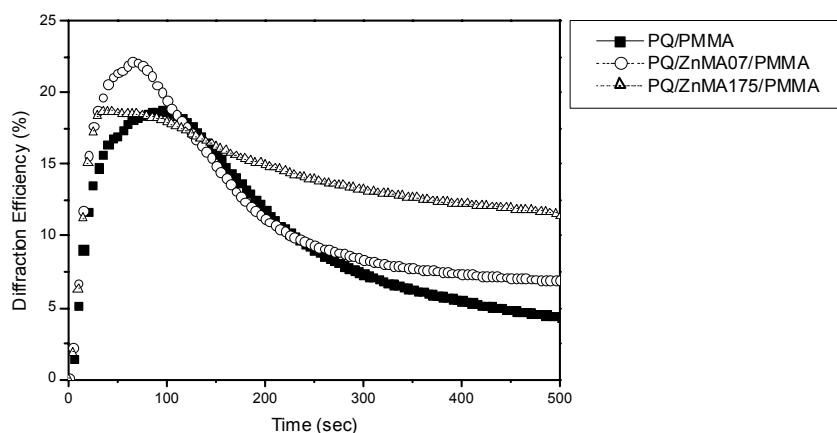
Table 2 Time constants pumped by 514 nm and probed by 632nm

It is seen from Table 2 that, for the samples with 5% weight of ZnMA, when concentrations of PQ is increased from 0.5% to 5% weight, time constant τ_1 is reduced from 98 sec to 25sec and τ_2 from 447sec to 145 sec, respectively. It indicates that the photoreaction becomes faster as the PQ concentration is increased. The higher doped concentrations of both ZnMA and PQ molecules produce the larger influence on the photoreaction at 514nm, and ZnMA appears more influential than PQ in enhancing the transmittance change of the samples. By these experiments, we knew that our samples the PQ molecule not only serves as photosensitive dye but also provides refractive index change via photoreaction with ZnMA molecule. The results indicate that in our samples the influence of photoreaction induced by ZnMA molecule is larger than that of PQ such that addition of ZnMA molecules into PQ/PMMA polymer is effective way to improve the sensitivity of our sample.

4.3 Holographic experiments

We have performed holographic recording experiments using different samples. The diffraction efficiencies as a function of recording time are shown in Fig 7. The maximum diffraction efficiency and the time to reach the maximum value are listed in Table 3.





(b)

Fig. 7 The diffraction efficiencies of the photopolymer. (a) 100 μ m films, (b) 2mm samples

It can be seen in Fig.7 (a)(curve marked by \blacksquare and \circ) that adding small amount of ZnMA dopant in PQ/PMMA can increase the diffraction efficiency of the holographic recording,. Response speed is also improved as the time constant is reduced from 102 sec to 86 sec, shown in Table 3. When the concentration of ZnMA is increased to 5% weight (curve marked by ∇), the diffraction efficiency of the hologram becomes lower than that of pure PQ-doped PMMA sample. The recording speed, however, is still improved, from 86 sec to 59 sec. It is because that the higher concentration of the ZnMA dopant produces the more photoreaction between PQ and ZnMA¹⁰. As a result, the speed of holographic recording becomes faster, but at the same time the material becomes more absorptive and the diffraction efficiency is decreased. Fig.7 (b) shows the diffraction efficiency of photopolymer of 2 mm thickness. It is seen that when 0.07% weight ZnMA is added into the PQ/PMMA photopolymer, the maximum diffraction efficiency rises up and is higher than that of pure PQ doped PMMA (compare curves marked by \blacksquare and \circ). As the concentration of ZnMA is increased to 0.175% weight, the diffraction efficiency the maximum diffraction efficiency is decreased, similar to that of the pure doped PMMA. However, the time constant for hologram recording is reduced from 96.2 sec to 42.3 sec, as shown in Table 3. This again confirms the role of ZnMA in speeding up the photoreaction of the material.

Samples	Thin films (100 μ m) (doctor-blade method)					Thick sample (2mm) (Thermo-polymerization)		
	ZnMA = 5 % weight		PQ = 5 % weight			PQ = 0.7 % weight		
	ZnMA5 /PQ0.5	ZnMA5 /PQ5	PQ	PQ5 /ZnMA0.5	PQ5 /ZnMA5	PQ0.7	PQ0.7/ZnMA 0.7	PQ0.7/ZnMA 0.175
Max. Diffraction Efficiency (%)	0.02	0.38	0.57	1.61	0.38	18.78	22.15	18.73
Time to reach η_{max} (sec)	96	59	102	86	59	96.2	66.3	42.3

Table 3 The maximum diffraction efficiency and time constant

It can be seen in Table 3 that, for the 100 μ m thin film samples, when the ZnMA concentration is fixed at 5% weight and the PQ concentration from 0.5% weight to the 5% weight, the response time is decreased from 96 sec to 59 sec and the maximum diffraction efficiency increases from 0.02% to 0.38%. It indicates that PQ plays an important role in forming holograms. On the other hand, when PQ concentration is fixed at 5% and ZnMA concentration is increased from 0% weight to 5% weight, the time constant is decreased from 102 sec to 59 sec. It is almost reduced by 1.77 times. But the diffraction efficiency is decreased from 0.57% to 0.38%. As explained in previous paragraph, this is because the material becomes too much absorptive. When the ZnMA concentration is added only 0.5% weight, then the diffraction efficiency becomes 1.61%, which is 3 times that of pure PQ/PMMA. These results imply that PQ molecules are responsible for the refractive index change for forming hologram recording, and ZnMA are responsible for the intermediate state of holograms recording. A small amount of ZnMA molecules serves as a catalyst to accelerate the photoreaction of PQ molecules. Thus, an optimization condition for the material then can be proposed as : adding a suitable amount of ZnMA to increase the recording sensitivity, and a suitable concentration of PQ to increase the diffraction efficiency. The chemical analysis of photoreaction in ZnMA/PQ/PMMA is under investigation and optimal condition for material composition will be provided in the future.

5. CONCLUSION

We have fabricated organometallic compound ZnMA doped PQ/PMMA photopolymer and investigated its optical and holographic characteristics. The transmittance measurements show that doping ZnMA into PQ/PMMA can reduce the time constant of photoreaction. Measurements on hologram recording show that not only response time but also diffraction efficiency can be improved by properly doping ZnMA concentration. Measurements indicate that PQ molecules mainly serve as photosensitive dye and ZnMA serves as a catalyst in ZnMA/PQ/PMMA photopolymer. Our results show that Zinc-organic compound or other organo-metallic compounds can be useful dopants to improve PQ/PMMA photopolymers for holographic recording.

6. ACKNOWLEDGEMENT

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