Influence of fabrication conditions on characteristics of phenanthrenequinone-doped poly(methyl methacrylate) photopolymer for holographic memory

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ABSTRACT

In this paper, we experimentally investigate the influence of the fabrication conditions on holographic characteristics in phenanthrenequinone-doped poly(methyl methacrylate) (PQ:PMMA) bulk photopolymer. In our investigation, the PQ:PMMA bulk samples are fabricated by use of a two-step thermo-polymerization method. We firstly propose to monitor relative viscosity of the monomer solution during the sample preparation to obtain a reliable criterion for material fabrication. We then compare experimentally characteristics of 2-mm thick samples fabricated with different conditions for holographic memory. The results show that the conditions in the first step play a important rule for fabricating bulk PQ:PMMA samples with good optical uniformity. In addition, the conditions in the second step play the rule for controlling the concentration of residual monomer and determine holographic characteristics. These results can provide a useful rule for fabricating bulk PQ:PMMA photopolymers for further applications on volume holographic data storage.

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. Currently, this technology is on the horizon for commercial applications, but is still rich for research activities [1–4]. Among the various aspects, finding a suitable volume holographic material is one of the most important issues. More recently, the research efforts have been shifted to photopolymer materials, because their fabrication is less involved and costly. Modifying the material components and fabrication procedures to fit into requirements of different applications is simpler [5–10]. However, in the most photopolymer materials, the modulation of the index of refraction for holographic recording is caused by photochemical polymerization, which often unavoidably causes significant local variation of the volume and consequently induces a strong material shrinkage during holographic recording. It leads to a loss of Bragg condition of readout beam such that the recorded information cannot be

read out completely [10]. This phenomenon becomes more severe as the material thickness is increased for achieving larger storage capacity. Thus, one of the fundamental keys for material development is the availability of low photo-induced shrinkage property.

Recently, a kind of diffusion amplification photopolymer material, named as PQ:PMMA which is a composite of phenanthrenequinone-doped poly(methyl methacrylate) has been shown to be a promising candidate for alleviating the shrinkage problem [11–18]. The doped elements in these materials are used for recording holograms, instead of the photoinduced polymerization or crosslinking mechanism. The polymerization of monomers in these materials is only used to make a strong polymer matrix for supporting thickness and optical quality of medium. The mechanism for recording hologram in PQ/PMMA is produced by the photochemical reactions involved with photosensitive elements; in this case PQ as well as residual monomers, MMA and polymer chain, PMMA. Hence, the key to achieve this goal lies in the material fabrication conditions to control the concentration of the residual monomer for photoreaction elements. It has been successfully demonstrated to fabricate few-mm-thick PQ/PMMA photopolymers by use of a two-step thermo-polymerization technique. The experiments show that the samples have indeed ultralow shrinkage and refractive index change comparable to other photopolymer materials [15–18]. However, the precise influence of the fabrication conditions in each step to the optical and holographic

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characteristics of the samples has yet to be unambiguously established. In this paper, we present experimentally influence of preparation conditions to the PQ:PMMA photopolymer samples. We first present how the fabrication conditions in the first step affect the optical quality of bulk sample and propose a criterion to choose the conditions by measuring the relative viscosity of the monomer solution during the sample preparation. We then characterize PQ:PMMA samples prepared with different fabrication conditions to identify the key factors of determining the characteristics of the samples for holographic memory. These two experimental results provide a useful rule for determining fabrication conditions and optimizing characteristics of thick PQ:PMMA samples for volume holographic memory.

2. The fabrication of thick PQ:PMMA photopolymer samples

Our two-step thermo-polymerization to fabricate bulk PQ: PMMA samples usually starts with raw materials: liquid monomer MMA, photo-sensitizer PQ, and thermo-initiator AIBN (2,2-Azo-bisisobutyrolnitrile). In the first step, the thermo-initiator AIBN ($\sim$ upto 2.0 wt. %) and PQ molecules ($\sim$ 0.7 wt%) are dissolved in solvent MMA. The solution is stirred (using a magneto stirrer) in a glass bottle at certain temperature (hereafter, named as stirring temperature) for a certain period (stirring time) until it becomes homogeneously viscoid. In the second step, the viscoid solution is injected into a glass mold, and then put it in an oven which is kept at higher temperature (baking temperature) to accelerate the polymerization process. After certain period (baking time), the sample become a self-sustained solid block, and can be removed from the mold for optical testing and holographic applications without post processing.

In experiments, we found that these two steps are necessary to fabricate samples with good optical quality. The purpose of first step is to dissipate N$_2$ gas from the thermo-decomposition of AIBN and huge amount of heat from radical generation of MMA monomers during the initial stage of thermo-polymerization of MMA. When they are released completely from the MMA solution, bubble-free bulk sample can be fabricated so that optical quality of the sample can be good enough for experiments. Thus, in the first fabrication step the solution was stirred (using a magneto stirrer) in a glass bottle at low temperature one could ideally obtain a sticky solution with clear phase. This sticky solution is injected into a glass mold to form a self-sustainable bubble-free block in the second step. To confirm these descriptions, we fabricated two samples using different stirring time at 30 °C in the first step and baking time of 5 days at 45 °C in the second step. The pictures of the final polymer samples are shown in Fig. 1. It is seen that the PQ:PMMA polymer bulk in the right bottle, which was stirred for 16 h has clear phase and uniform transparency. The bulk in the left bottle, which had not proceeded in the first step (zero-h stirring) seems to deliver a very distorted shape with unacceptable optical quality. Concerning these points, it is obvious how to choose the timing to possess molding in the second step plays a critical rule for our two-step method.

One can observe that the liquid solution becomes thicker and thicker as a result of the polymerization of liquid MMA initiated by AIBN. Thus, the viscosity of the solution is a good indicator for choosing timing under different temperature. For the experimental confirmation, we fixed the stirring temperature at 30 °C and used the stirring time as parameter to determine timing. A quantitative relationship between the viscosity of the MMA solution and stirring time, t_s is measured. It can be performed by an Ubbelohde capillary (as illustrated in Fig. 2 (a)) bathed in 30 °C water. In experiments, γ hole was sealed and the MMA solution was injected to the bottom vessel through α hole until the surface
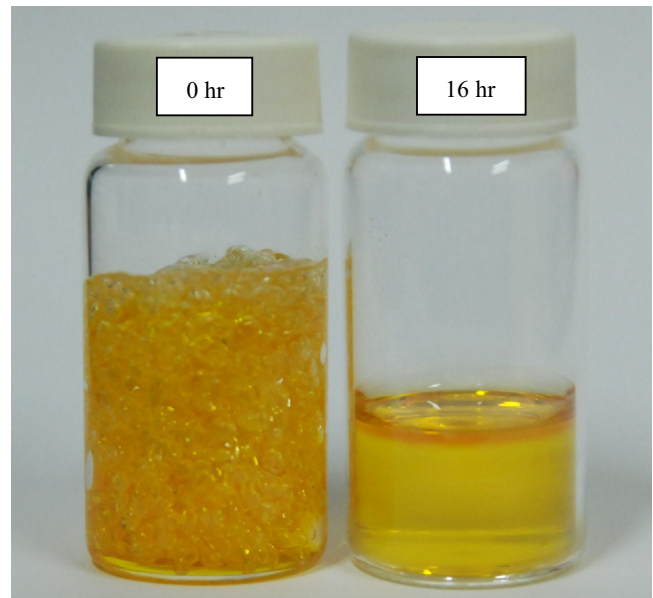

Fig. 1. The pictures of the PQ/PMMA polymer in the sample bottle with different first step stirring time 16 h and 0 h.

of the solution was over A line. The β hole and the z side of the vacuum suction were then connected. The solution was draw to vessel on right-hand side by the suction until the surface of solution was over B line. When the y side was turn on to depress suction, the surface of solution was falling because of the gravity and the falling time from B to C line was measured. In a linear approximation, the falling time is proportional to the viscosity of the liquid. The relative viscosity can be expressed as: $\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$, where η, ρ, and t represent viscosity, density, and falling time of sample solution under different string time, respectively, and η_0, ρ_0, and t_0 represents the corresponding parameters of a reference liquid. In our case, it is the MMA solvent. By measuring the falling time of the sample and MMA solutions, the relative viscosity of the solution under different string time can be determined assuming that the density ρ and ρ_0 are the same during material preparation. The experimental results of viscosity measurement are summarized and plotted in Fig. 2(b). It is seen that when the stirring time is less than 16 h, the relative viscosity remains a small value, further increases rapidly. This result implies that polymerization is speeding up due to propagation of polymer chain after 16 h. By eye visual, it was seen that the solution started to become sticky. In addition, in experiments, we found that when the stirring time is longer than 16 h, the baking temperature and time in the second step were not critical issues to obtain bulk PQ:PMMA sample with good optical quality, as long as the baking temperature is much less than the boiling temperature of MMA solution ($\sim$110 °C). Furthermore, when the stirring time is over 24 h, the solution becomes too sticky to take the solution out of the glass bottle. Thus, it concludes that the timing to reach at high growing rate of the relative viscosity, which represents high thermo-polymerization rate, can be chosen to proceed the second step for molding samples. At 30 °C, the period between 16 h and 24 h which produces the relative viscosity of solution in the range of $\eta_r = 10 \sim 110$ is acceptable.

On the other hand, this acceptable relative viscosity can be used as a criterion to determine timing when the stirring temperature is changed. For a chemical reaction, the relation between the speed of reaction and experimental conditions can usually be determined by using Arrhenius equation [22,23]. Thus, for our case, the temperature dependence of the stirring time, t_s to
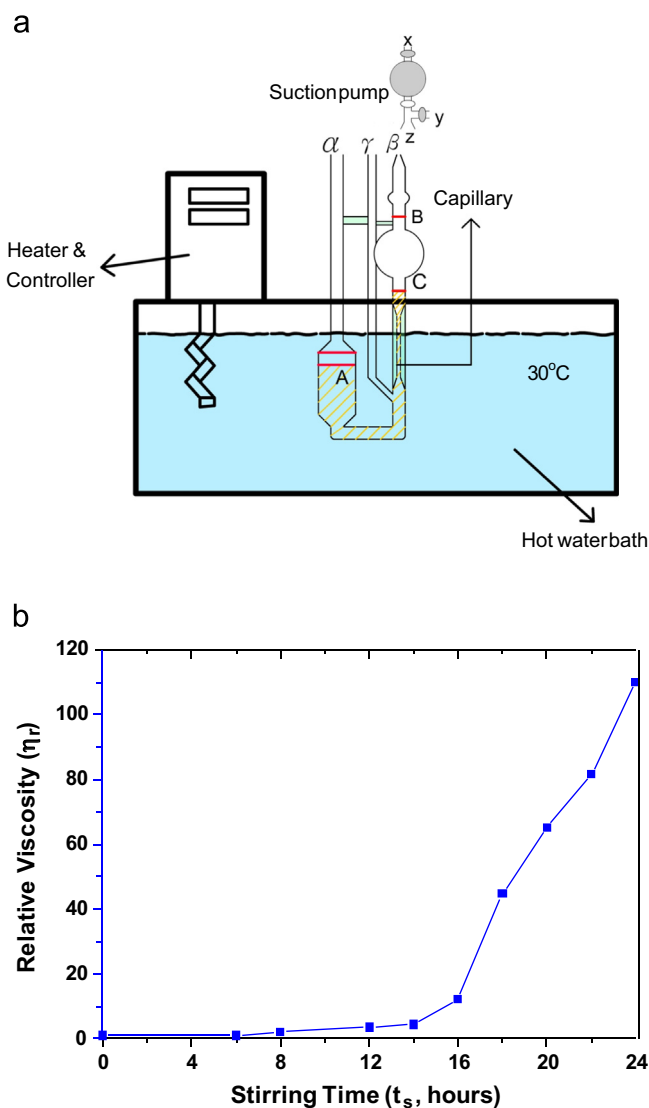
a

b

Fig. 2. (a) The Ubbelohde capillary (b) The relative viscosity as function of the stirring time. The symbols represent measured results, and the curves are guides for the eye.

approach the same relative viscosity, can be described by the relation, $\ln t_s = \frac{E_a}{RT} - \ln A$, where T is temperature, A is the pre-exponential factor, E_a is activation energy of reaction and R is the ideal gas constant. From experiments, the stirring times, for achieving $\eta_r = 110$ at 30 °C, 45 °C and 60 °C were obtained as 1440, 850, 240 minutes, respectively. Therefore, the fitting results show that the parameters of A and E_a are 3.738×10^{10} min^{-1} and 79.4 KJ mol^{-1}. With these two parameters, Arrhenius equation can be useful to predict the stirring time at a given temperature in the first step. It yields a well-conditioned solution to choose the timing for facilitating molding a bulk sample for obtaining good optical quality.

Since baking temperature and time is not critical for optical quality, we fixed the baking temperature to be 45 °C and used the baking time as a parameter for testing influence of the fabrication conditions on the holographic characteristics of the samples. We fabricated a set of 2-mm thick samples with 1 wt% of AIBN and 0.7% of PQ using different stirring time and temperature at the first step, different baking time at the second step. The other set of samples were fabricated using different concentration of AIBN. The conditions are summarized in Tables 1 and 2.

Table 1
The fabrication conditions of different PQ/PMMA sample.

Sample #	Stirring temperature (°C)	Stirring time (h)	baking temperature (°C)	baking time (h)
1	30	8	45	72
2	30	16	45	72
3	30	18	45	72
4	30	24	45	72
5	45	14	45	72
6	60	4	45	72
7	30	24	45	48
8	30	24	45	72
9	30	24	45	96
10	30	24	45	120

Table 2
$M\#$, E_r and S of samples fabricated with the stirring time of 24 h at 30 °C and the baking time of 3 days at 45 °C, but with different concentrations of AIBN.

AIBN conc.(wt%)	$M\#$	E_r (J/cm^2)	S (cm^2/J)
0.5	1.23	10.33	0.12
1	2.11	8.93	0.24
2	3.41	12.82	0.25

3. Experimental characterization of PQ:PMMA samples for holographic memory

3.1. Volume hologram recording capability

The first experiment is to test the volume hologram recording capability of our photopolymer samples. A plane-wave hologram was recorded in a 2-mm-thick sample by a pair of 514-nm beams, each with the intensity of 30 mW/cm^2, incidents at an intersection angle of 30° outside the material. The exposure time was about 10 s and the diffraction efficiency of the hologram reached ∼10%. After recording, we monitored the Bragg selectivity curve of the hologram by rotating the sample mounted on a rotational stage. Diffraction efficiency of the hologram was plotted as a function of rotational angle. Fig. 3 shows a typical example from measurements for different samples. It can be seen clearly that the hologram has a sinc-squared selectivity curve as expected for a 2-mm-thick hologram. This result indicates that the shrinkage effect in our PQ:PMMA sample is small enough to be neglected, because we are able to reconstruct high-bandwidth holograms completely. Thus, our two-step thermo-polymerization method is suitable to produce PQ:PMMA photopolymer for volume holographic applications.

3.2. Material dynamic range and sensitivity

The second experiment is to test capability of the material for holographic memory. We used the slightly modified recording geometry. In experiments, the sample was fixed on a rotational stage and the surface of sample was perpendicular to the rotational axis. Peristrophic multiplexing technique was applied to record 200 plane-wave holograms in one location of the photopolymer [19]. The exposure energy density for each hologram was 0.21 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 at the cumulative exposure energy E(J cm^{-2}) of each hologram. By curve

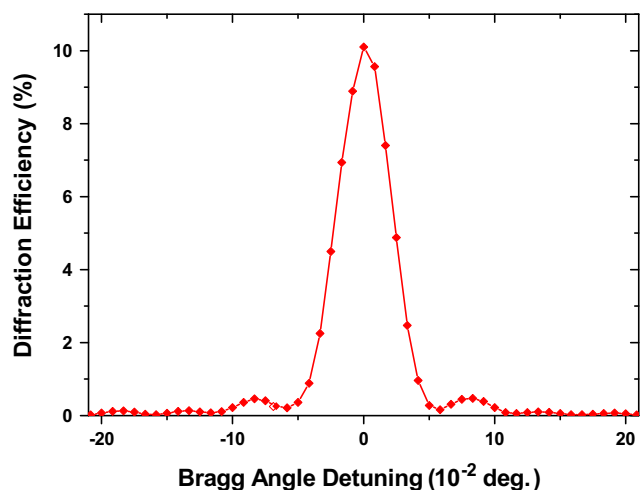**Fig. 3.** The Bragg selectivity curve for a hologram with diffraction efficiency of ~10% in a 2-mm-thick sample.

fitting with the function: $C(E) = C_{sat}[1 - \exp - (E/E_\tau)]$, 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 respective to the amount of exposure energy. When the sample is unexposed, $S = \left.\frac{dC(E)}{dE}\right|_{E\to 0} = \frac{M\#}{E_\tau}$, according to the running curve function. The $M\#$ and S are two of most important factors to evaluate the capabilities of the photopolymer, including storage capacity and recording data rate for holographic data storage [20].

3.2.1. The influence of stirring time and temperature

The running curve of the cumulative grating strength for different samples, which were fabricated using different stirring time at 30 °C in the first step and 3-day baking time in the second step (samples #1–4 in Table 1) are shown in Fig. 4 (a). The experimental results of $M\#$ and S for those samples are summarized in Fig. 4 (b). Moreover, the running curves for samples fabricated with different stirring time at different temperature to keep the similar relative viscosity ($\eta_r \sim 110$, samples #4–6 in Table 1) in the first step and 3-day baking in the second step is shown in Fig. 5. In both cases, the $M\#$ and S are improved very slightly. It indicates the stirring time and temperature are not critical issues for determining holographic characteristics of material for optical memory. The reason could be attributed to the fact that with the same baking processing in the second step, the amount of the residual MMA molecules for photo-reaction is almost the same in those samples. According to our previous investigations [21], the physical mechanism of holographic recording in our PQ/PMMA is attributed to the photo-induced radical generation of PQ and the resulting chemical attachment with the residual MMA, and this structural change of the PQ molecule produces a refractive index change to form the phase grating. If the concentration of MMA was left with the similar amount during material preparation, the holographic characteristics of the samples will be similar. For this reason, we anticipate the baking time at certain baking temperature should play main factor for determining holographic characteristics of the sample.

3.2.2. The influence of baking time

We performed the same measurements for the different samples fabricated with the same stirring time (~24 h, at 30 °C) in the first step and different baking time in the second step (samples #7–10 in Table 1). Fig. 6(a) shows the experimental
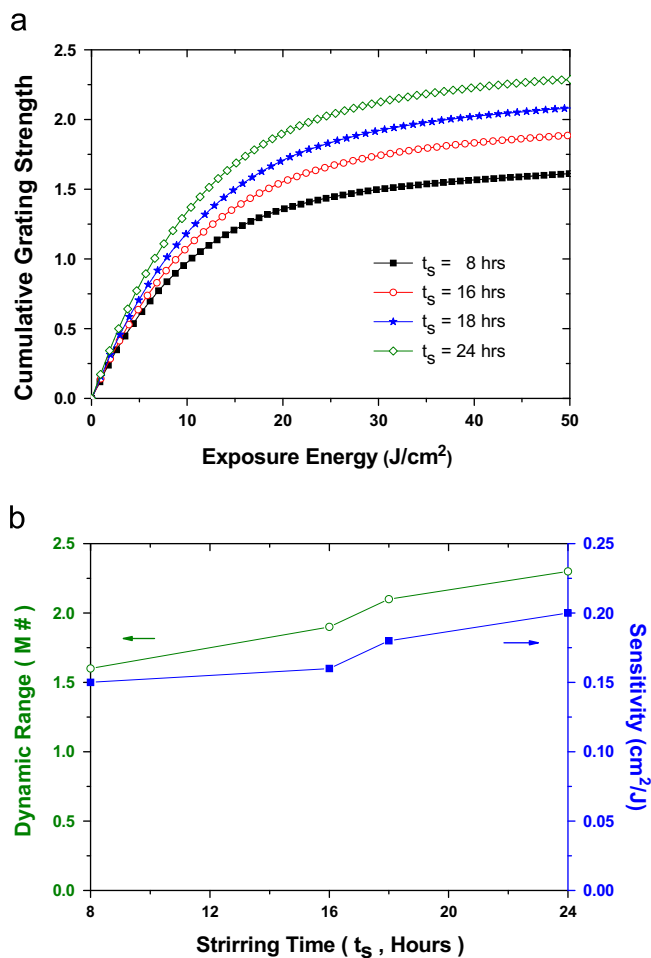

Fig. 4. (a) The running curves of the cumulative grating strength as a function of the cumulative exposure energy, (b) the experimental results of $M\#$ and S, for samples fabricated with different stirring time in the first step and 3-day baking in the second step. The symbols represent measured results, and the curves are guides for the eye.
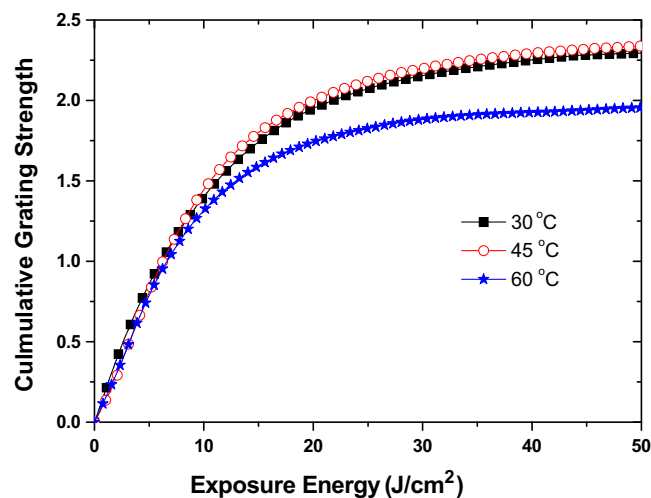

Fig. 5. The running curves of the cumulative grating strength as a function of the cumulative exposure energy for samples fabricated with same relative viscosity in the first step and 3-day baking in the second step.

running curves of cumulative grating strengths for different samples. The experimental results of $M\#$ and S for those samples are summarized in Fig. 6(b). As is illustrated, the $M\#$ of different samples dramatically decreases with the baking time, and the S
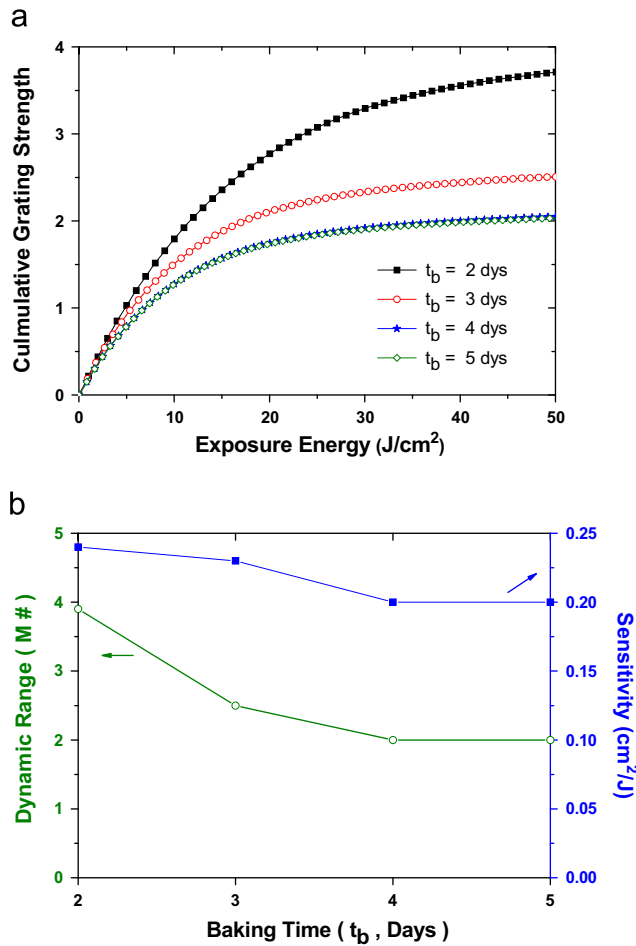
Fig. 6. (a) The running curves of the cumulative grating strength as a function of the cumulative exposure energy, (b) the experimental results of M# and S, for samples fabricated with 24-h stirring in the first step and different baking time in the second step. The symbols represent measured results, and the curves are guides for the eye.
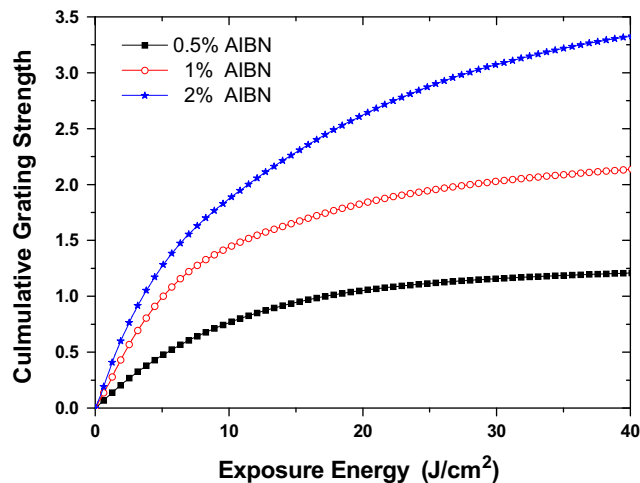

Fig. 7. The running curves of the cumulative grating strength as a function of the cumulative exposure energy for samples fabricated with different concentrations of AIBN.

changes only slightly. For the samples with the baking time larger than 4 days, running curves remain almost the same and so are M# and S. The results closely meet with the conclusion of the first measurements. Under fixed baking temperature, the baking time

plays the key factor for controlling the concentrations of the residual monomer during material preparation and thus determines holographic characteristics of the sample. Once the baking time is long enough to form hard polymer matrix for fabricating bulk PQ:PMMA sample, the shorter baking time provides the larger M/# of sample. However, it may not be appropriate to have shorter baking time (like 2 days), although the sample may have better dynamic range. It because that the baking temperature in our case is kept at 45 °C so that the thermo-polymerization of polymer matrix PMMA is not complete yet. The MMA molecules are still depleted after the samples are taken out from oven. Thus, the shelf life of sample to remain higher dynamic range will be expected to be shorter when the baking time is too short. After fabrication, the achievable M/# of these samples will decrease as the time goes.

3.2.3. The influence of the concentration of thermo-initiator, AIBN

Another issue has to be examined is the concentration of thermo-initiator, AIBN, because it affects the degree of polymerization of the sample and then gives different surrounding matrix environment for photoreaction of PQ and residual MMA molecules. Thus, we use the conditions of 24-h stirring at 30 °C and 3-day baking at 45 °C to fabricate the samples with different concentration of AIBN, changing from 0.5 to 2.0 wt%. The same holographic characterization has been performed. Fig. 7 shows the running curves for different samples. As is illustrated, the M# of the material increases with concentration of AIBN. By curve fitting, the E_τ and S of the samples can be obtained and listed in Table 2. It can be seen that E_τ of the samples change slightly, but the sensitivities of samples have been improved by 2.08 times, from 0.5 wt% to 2.0 wt % of AIBN due to the improvements of the dynamic range with 2.77 times. The result indicates that the fabricated samples with higher concentration of AIBN have an efficient surrounding matrix for holographic recording. It is because that higher concentration of AIBN, the shorter PMMA polymer chains. The structure of polymer matrix becomes looser and the amount of residual MMA is larger such that the photo-reaction of PQ and residual MMA molecules occurs easier. Thus, improvements of dynamic range and sensitivity of the samples for holographic recording become considerable. However, the sample with higher concentration of AIBN can be expected to have lower glass temperature such that the mechanic strength of the sample is reduced. The trade-off between these different factors could be made for the requirements of different applications using the above experimental results and discussions.

4. Conclusion

Combining the measurement of relative viscosity during material fabrication and experimental results of holographic characterization, we can obtain a rule for a two-step thermo-polymerization method to make PQ:PMMA photopolymer. At first, the stirring time and temperature in the first step should be chosen by using the Arrhenius equation such that the relative viscosity of the solution reaches to the range of $\eta_r = 10 \sim 110$, when the polymerization of MMA starts to speed up. The N_2 gas produced by the decomposition of AIBN and heat produced by the radical generation can be released from the mold completely for obtaining bobble free PQ:PMMA photopolymer bulk. It is important because the sample can be used for optical testing and holographic application without any post processing. Second, the baking time in the second step plays the key role for controlling the concentration of the residual MMA such that the holographic characteristics of sample for optical memory are determined by the baking time. As long as the solution can be transferred into the solid bulk,

the shorter baking time give rise to the larger $M/\#$ of the sample. The achieved largest value for 2-mm thick sample is around 3.9. Since the $M/\#$ is proportional to the thickness of the sample [1], it can be further improved by increasing the thickness of sample and using the optimized fabrication conditions. In addition, the concentration of thermo-initiator also plays a role for controlling the concentration of the residual MMA and length of PMMA polymer chain. The higher concentration gives to the larger M/# of the sample. These results can provide a useful rule for fabricating bulk PQ:PMMA photopolymers for further applications on volume holographic data storage.

Acknowledgments

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