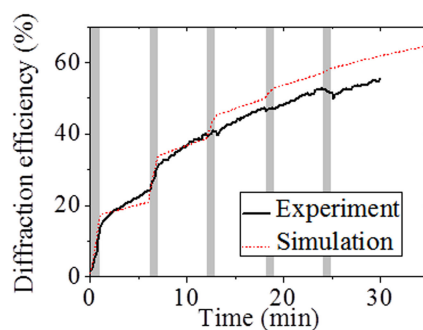


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Bao-Jen Shih
Cuan-Wen Chen
Yu-Hua Hsieh
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Bao-Jen Shih ¹, Cuan-Wen Chen,¹ Yu-Hua Hsieh,¹
Te-Yuan Chung ¹ and Shiuian-Huei Lin²

¹Department of Optics and Photonics, National Central University, Taoyuan 32001, Taiwan, R.O.C

²Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C

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Abstract: A simulation based on the rate equations was performed to analyze the concentration distribution of molecules in phenanthrenequinone (PQ) doped polymethyl methacrylate (PMMA) polymers (PQ-PMMA) exposed using a two-beam interference configuration. The concentration distributions were used to predict the diffraction efficiency of PQ-PMMA-based volume Bragg gratings (VBGs) by using the transfer matrix method. The simulation results suggest that an intermittent exposure method can promote the diffusion of PQ molecules and increase the final diffraction efficiency. A series of experiments validated our hypothesis that the diffraction efficiency of reflective-type PQ-PMMA VBG can be predicted.

Index Terms: Bragg gratings, holographic optical components, optical polymers.

1. Introduction

Photopolymer materials are suitable for the holographic write-once-read-only-memory system because it is easy to fabricate and can provide large modulation in refractive index [1]. Among such materials, Phenanthrenequinone (PQ) doped poly methyl methacrylate (PQ-PMMA) plays an important role because of its high optical quality and negligible photoinduced shrinkage. The PQ molecules react with the host polymer matrix PMMA or its monomer MMA to change the refractive index after exposure to green or blue illumination [2], [3]. When a PQ-PMMA photopolymer is exposed to a sinusoidal intensity light pattern, a periodical refractive index distribution forms in the material which becomes a volume Bragg grating (VBG). Such PQ-PMMA VBG can serve as a low-cost yet powerful optical element. However, it is difficult to predict the diffraction efficiency of a homemade reflective-type PQ-PMMA VBG because it is difficult to obtain every parameter accurately, and the parameters in previous researches may not be suitable for use because of different production process and different experimental demand. In order to design a reflective-type PQ-PMMA VBG practically and conveniently, in this work, a set of simplified chemical rate equations with diffusion is proposed to simulate the diffraction efficiency of reflective-type PQ-PMMA VBGs.

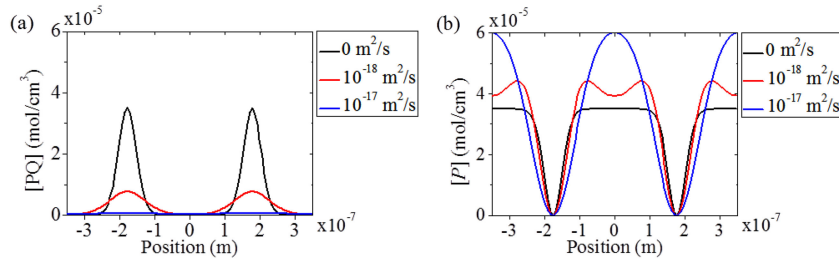


Fig. 1. The simulation results for (a) $[PQ(x, t)]$ and (b) $[P(x, t)]$ for different D_{PQ} when $t = 5000$ s, $[PQ(x, 0)] = 3.5 \times 10^{-5}$ mol/cm³, $k_p I_0 = 10^{-3}$ 1/s, and $\Lambda = 354$ nm.

2. Simulation Methods

Chemical rate equations of photochemical mechanisms can be used to simulate the concentration distribution of molecules in PQ-PMMA samples [4], [5]. When the PQ is illuminated by 532 nm light, the ground state PQ molecule will absorb photons and will be excited to the singlet state, $^1PQ^*$. Following this, $^1PQ^*$ can be converted into the more stable triplet state, $^3PQ^*$, through an intersystem-crossing process. Furthermore, $^3PQ^*$ can combine with MMA monomers or the PMMA matrix to produce a photoproduct, P . Although both $^1PQ^*$ and $^3PQ^*$ can return to the ground state PQ, recovery rates are slow [6] and can thus be neglected. In addition, the rate of the excitation process is much slower than the rate of both the intersystem-crossing process and the combining process. Therefore, $^1PQ^*$ can be combined directly and instantaneously with the abundant MMA or PMMA. The chemical equations for the resultant photochemical mechanisms are



where $k_p I(x)$ is the rate coefficient of the promoting process; $I(x)$ is the light intensity along the x -axis and can be defined as

$$I(x) = I_0 \left[1 + \cos\left(\frac{2\pi}{\Lambda}x\right) \right], \quad (4)$$

where I_0 is the light intensity; Λ is the grating period; k_p is the constant which represents the excitation rate coefficient per unit light intensity in units of cm²/mW·s. k_c is the reaction rate constant of the combining process, and the value of k_c is extremely large so that the reaction is almost instantaneous. In addition, the MMA and PMMA concentrations are assumed to be much higher than that of the PQ and remain almost unchanged in the reaction [7]. Meanwhile, the PQ molecules can diffuse within the PMMA matrix. This diffusion allows the PQ in the low illumination region to diffuse to the high illumination region to generate more photoproduct. Therefore, the chemical rate equations with diffusion can be written as

$$\frac{\partial [PQ(x, t)]}{\partial t} = \frac{\partial}{\partial x} D_{PQ} \frac{\partial [PQ(x, t)]}{\partial x} - k_p I(x) [PQ(x, t)], \quad (5)$$

$$\frac{\partial [P(x, t)]}{\partial t} = k_p I(x) [PQ(x, t)], \quad (6)$$

where $[PQ(x, t)]$ and $[P(x, t)]$ are the concentration distributions of PQ and P , respectively; D_{PQ} is the diffusion coefficient of the PQ molecules. Fig. 1 shows the simulation results for $[PQ(x, t)]$ and $[P(x, t)]$ for different D_{PQ} . For a non-diffusive case ($D_{PQ} = 0$), PQ is depleted and P forms in the illuminated regions. As the fluence accumulates, the concentration of P in the more weakly

illuminated regions also reaches the maximum possible value, so that $[P(x, t)]$ becomes a plateau-shaped curve. For very fast diffusion ($D_{PQ} = 10^{-17}$ m²/s), $[P(x, t)]$ is very similar to a sinusoidal function as the PQ diffuses into the high illuminated regions, and P forms rather quickly. However, if the diffusion is not as fast as in the previous case ($D_{PQ} = 10^{-18}$ m²/s), PQ can absorb light on the way through diffusion from the regions with lower illumination to the high illuminated regions to form the product. As a result, $[P(x, t)]$ acquires an interesting M-shaped curve. The simulation results indicate that a higher D_{PQ} causes the curve of $[P(x, t)]$ to more like a sinusoidal function and leads to a higher grating strength for P . The grating strength of PQ is out-of-phase with respect to that of P which leads to a lower total grating strength. Nevertheless, the diffusion of PQ molecules reduces the grating strength of PQ, and eventually, the total diffraction efficiency is dominated by only the grating strength of P . Therefore, a higher D_{PQ} leads to a higher total grating strength in general.

To calculate the diffraction efficiency, the refractive index distribution, $n(x, t)$, is required. Based on the Lorentz–Lorenz approach [8], the refractive index of the PQ-PMMA can be written as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_{PQ}^2 - 1}{n_{PQ}^2 + 2} \varphi_{PQ} + \frac{n_P^2 - 1}{n_P^2 + 2} \varphi_P + \frac{n_B^2 - 1}{n_B^2 + 2} \varphi_B, \quad (7)$$

where n_{PQ} , n_P , and n_B are the refractive indexes of PQ, P , and the background (all the other components in the material), respectively; φ_{PQ} , φ_P , and φ_B are the volume fractions of PQ, P , and the background, respectively. With the assumption of a low PQ concentration, φ_B is much larger than both φ_{PQ} and φ_P . In addition, the value of n_B is very close to n [7], and the equation can now be derived as follows:

$$n = n_B + \frac{1}{2n_B} \left[\frac{(n_{PQ}^2 - 1)(n_B^2 + 2)}{(n_{PQ}^2 + 2)} - (n_B^2 - 1) \right] \varphi_{PQ} + \frac{1}{2n_B} \left[\frac{(n_P^2 - 1)(n_B^2 + 2)}{(n_P^2 + 2)} - (n_B^2 - 1) \right] \varphi_P. \quad (8)$$

With the additional assumption that the total volume does not vary (the PQ-PMMA sample does not shrink), φ_{PQ} is proportional to $[PQ(x, t)]$ and φ_P is proportional to $[P(x, t)]$. The refractive index distribution then can be simplified to

$$n(x, t) = n_B + \gamma_{PQ} [PQ(x, t)] + \gamma_P [P(x, t)], \quad (9)$$

where γ_{PQ} and γ_P are the coefficients which represent the refractive index change per unit concentration in units of cm³/mol. With the knowledge of the refractive index distribution, the diffraction efficiency of the PQ-PMMA VBG then can be calculated by the transfer-matrix method [9], [10] or by the coupled mode equations [11]. In this research, in order to calculate the diffraction efficiency of non-uniform gratings (which will be emerged in the sample because of absorption and long thickness), the simulated diffraction efficiency should be obtained by using transfer matrix method. The demanded parameters in the model are $[PQ(x, 0)]$, l_0 , Δ , D_{PQ} , k_p , γ_{PQ} , and γ_P . The values of $[PQ(x, 0)]$, l_0 , and Δ depend on the experimental configuration, and the others parameters can be obtained by fitting the experimental data.

3. Experimental Procedure

3.1 Experimental Setup

For the experiments, PQ-PMMA samples were prepared and polymerized following the procedure in Ref. [7] for use in homemade cells. The plate-shaped PQ-PMMA samples were 2 mm thick. The weight percentages of the PQ molecules, PMMA polymer, and residual MMA monomers in the sample were 0.7 wt.%, 89.3 wt.%, and 10 wt.%, respectively. A value of $[PQ(x, 0)] = 3.5 \times 10^{-5}$ mol/cm³ can be estimated from the initial composition. The refractive index of PQ-PMMA sample is 1.493 [4]. In the experiments, the PQ-PMMA sample was sandwiched between two BK7 prisms, and the interface between the sample and the prisms was filled with silicone oil which served as the index-matching material to reduce surface reflection and improve optical quality. The

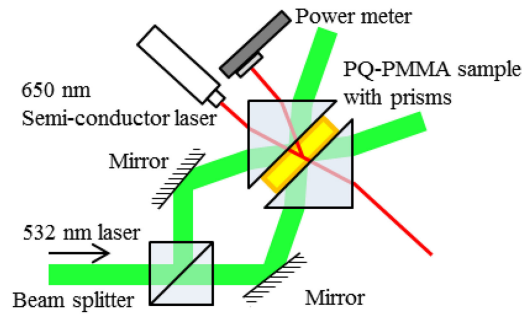


Fig. 2. The two-beam interference configuration.

prisms changed the refraction angle which made it possible to obtain larger grating periods than that without the prisms. The sample with prisms was placed at the intersection of a two-beam interference configuration as shown in Fig. 2. The recording wavelength was 532 nm. The two beams passed through the prisms and entered the sample from the opposite side at the same incident angle. The grating period, Λ , was set to be 354 nm, which made the Bragg wavelength (the wavelength for diffraction at a normal incident angle) 1055 nm since Bragg's condition $m\lambda_B = 2n\Lambda\cos\theta_B$. Since the PQ molecule is insensitive at a wavelength of 650 nm [7], a 650 nm beam was set for the Bragg condition and was used to monitor the diffraction efficiency during the experiments. The spectral width of 650 nm laser is 0.14 nm. In the further experiment, the spectrum width of VBG is measured to be 0.5–0.6 nm, so the 650 nm laser can be used to monitor the diffraction efficiency of the PQ-PMMA VBG.

3.2 Parameters

The value of D_{PQ} can be obtained by fitting the data in the dark reaction process (the reaction after exposure with only the diffusion effect of the PQ molecules carried out). The $[PQ(x, t)]$ can be Fourier decomposed in space. Only the 1st Fourier component influences the diffraction efficiency [11] and can be defined as

$$[PQ_1(x, t)] = A_{PQ}(t) \cos\left(\frac{2\pi}{\Lambda}x\right), \quad (10)$$

where $A_{PQ}(t)$ is the amplitude of the 1st Fourier component. The 1st Fourier component satisfies the diffusion equation and leads to

$$\frac{\partial [PQ_1(x, t)]}{\partial t} = \frac{\partial}{\partial x} D_{PQ} \frac{\partial [PQ_1(x, t)]}{\partial x}, \quad (11)$$

$A_{PQ}(t)$ can then be solved using Eq. (10) and Eq. (11) as follows:

$$A_{PQ}(t) = A_{PQ}(t_0) \exp\left(-D_{PQ} \frac{4\pi^2}{\Lambda^2} t\right). \quad (12)$$

Eq. (12) shows that the amplitude of the PQ decays exponentially during the dark reaction process. In the experiment, the sample was exposed for 24 mins with $I_0 = 60 \text{ mW/cm}^2$. Fig. 3 shows the diffraction efficiency as a function of time. Due to the dark reaction, the diffraction efficiency kept increasing even the exposure beam was switched off. From the fit of the experimental data in the dark reaction region, $D_{PQ} = 1.223 \times 10^{-18} \text{ m}^2/\text{s}$ could be obtained.

Knowing D_{PQ} , the value of k_p can then be obtained by taking the fit of the data under a different exposure I_0 . Fig. 4 shows the experimental results for I_0 of 60 mW/cm^2 , 120 mW/cm^2 , and 350 mW/cm^2 . By fitting the experimental data, $k_p = 1.75 \times 10^{-5} \text{ cm}^2/\text{mW}\cdot\text{s}$ is obtained.

In the experiments, the diffraction efficiency initially increases and then decreases later. The maximum value of the diffraction efficiency occurs when the exposure energy reaches about 110 J/cm^2 .

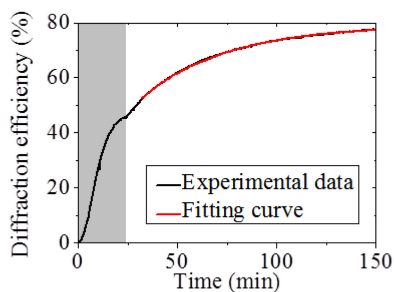


Fig. 3. The experimental results and the fitting curve for the progress of the dark reaction. The shaded region indicates the exposure period.

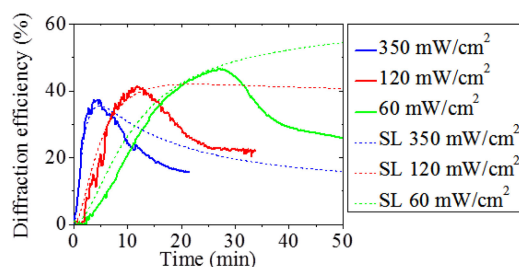


Fig. 4. The solid curves and the dashed curves represent the experimental and simulated (SL) results for I_0 equals 60 mW/cm², 120 mW/cm², and 350 mW/cm², respectively.

TABLE 1
The Comparison of Final Diffraction Efficiencies

	Predicted value	Experimental result
Consecutive exposure	76.6%	77.2%
Intermittent exposure	82.2%	87.4%

A lower I_0 makes the reaction slower, and the maximum value of the diffraction efficiency increases as I_0 decreases because it is easier for the PQ molecules to diffuse from the un-illuminated region to the illuminated region which causes the grating of P to become higher. It reveals that the diffraction efficiency can be different even if the total exposure energy is the same. After reaching the maximum value, the simulated curve shows a gradually mismatch to the experimental data. Such a discrepancy may be caused by several non-ideal effects such as noise grating and scattering from the sample or thermal effects during recording [12]. In addition, a longer exposure time amplifies any perturbation introduced from the environment and leads to a larger discrepancy. In order to reduce the complication, only total exposure energy of less than 110 J/cm² was considered in the following experiments.

Here, γ_P can be calculated from the final and stable diffraction efficiency which depends only on the P grating, because the PQ grating vanishes due to the diffusion effect. In the experiments, the final diffraction efficiency was measured from the sample after being stored for 1 day after exposure. The concentration of P molecules can be obtained by using the simulation method with known parameters I_0 , k_p , $[PQ(x, 0)]$, and D_{PQ} . Then by using Eq. 9 and couple mode equations, γ_P is found to be 5.61 cm³/mol. γ_{PQ} is calculated to be 2.9 cm³/mol based on the data obtained during the dark reaction period. The final diffraction efficiencies of simulation predicted value and the experimental value when I_0 was set to be 350 mW/cm² are shown in Table 1. The results from several experiments indicate that the difference between the simulation predicted value and the

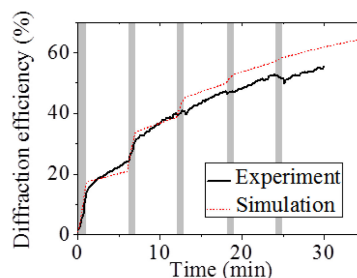


Fig. 5. The experimental and simulated results for the intermittent exposure experiment. The shaded regions indicate the exposure periods.

experimental value of final diffraction efficiency was within $\pm 3\%$ if I_0 was set to be 60–350 mW/cm^2 and the total exposure energy was less than 110 J/cm^2 .

3.3 Intermittent Exposure Method

Since the diffusion effect of PQ is the key determinant to reach high diffraction efficiency, it is better to choose a low I_0 which extends the diffusion time during the exposure. However, a longer exposure time introduces more perturbation from the environment. To simultaneously obtain a short exposure time and long diffusion time, an intermittent exposure method was proposed and performed. I_0 was set to be 350 mW/cm^2 . The total exposure time was set to be 5 min, but the light was turned off for 5 min for every 1 min of exposure. Fig. 5 shows the diffraction efficiency of the samples obtained using intermittent exposure method. The simulation curve does not match the experimental data well after 12 min during the writing and developing period. Some preliminary experiments suggest that the thermal effect may be responsible for this discrepancy. However, the experimental value of the final diffraction efficiency agrees relatively well with the prediction made by the proposed model. Table 1 shows the predicted values and the experimental results for the final diffraction efficiency using both the consecutive exposure and the intermittent exposure method. The total exposure time was set to be 5 min. The diffraction efficiencies of the intermittent exposure method are unmistakably higher than the results of consecutive exposure.

4. Conclusion

This study shows that the diffraction efficiency of PQ-PMMA VBG can be successfully predicted by using a simplified rate equation model, with an error within $\pm 3\%$ if I_0 is set to be 60–350 mW/cm^2 and the total exposure energy is less than 110 J/cm^2 . All the parameters demanded for this model can be obtained by fitting the diffraction efficiency to several experiments. Based on the model, the simulation results show that the diffusion effect of PQ is the most important factor that influences the final diffraction efficiency. Following these experiments, an intermittent exposure method is proposed and confirmed to be a practical method to increase the diffraction efficiency of PQ-PMMA VBG.

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