

# Investigation on the phase shifts of extinction and phase gratings in polymethyl methacrylate

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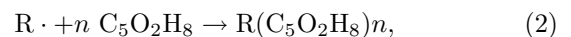
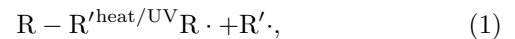
The phase shifts of the extinction and refractive index gratings to the illumination pattern are revealed in doped polymethyl methacrylate (PMMA). The dynamic process of these shifts is studied via two-wave coupling at 351 nm. It is shown that these shifts are from the strain and the shrinkage inside the sample and accompanied with the photo-repolymerization process during the building process of the holographic grating. Such shifts will cause obvious energy exchange between the two recording beams and enough attention should be paid to the nonlocal property of the holographic gratings of the material in the application.

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Organic materials have been introduced to the area of photonics for a long time<sup>[1–5]</sup>, among which polymethyl methacrylate (PMMA) is one of the most important for its perfect optical properties such as high transmission, excellent mechanical characteristics, and low cost<sup>[1]</sup>. New materials have been developed from PMMA by doping different functional impurities such as photoinitiator, light-induced isomer, fluorescence dye, and so on<sup>[6–8]</sup>. PMMA doped with 2,2-dimethoxy-2-phenylacetophenone (DMPA), which is a kind of ultraviolet (UV) photoinitiator, is very important and has been well studied for its abilities to record holographic gratings<sup>[9]</sup>. Recently, energy exchange in two-wave coupling was observed in DMPA-doped PMMA<sup>[10]</sup>, which was usually caused by the phase shifts between the holographic gratings and the illumination pattern. In this letter, we study the phase shifts in extinction and refractive index gratings and present their different contributions. By studying the phase shifts during the recording process of the gratings, we find that the phase shift is due to the strain and shrinkage in the photo-repolymerization of the incompletely reacted PMMA in the sample. Such phase shifts are not negligible and should be paid more attention to in applications such as optical communication and integrated optics with PMMA elements.

Because the recording of holographic gratings is based on photo-repolymerization in PMMA with monomers, it is necessary to review the chemistry process of the sample preparation and the photo-repolymerization firstly. Incompletely reacted PMMA could be polymerized from methyl methacrylate (MMA). With the help of thermo-initiator, PMMA bulk could be obtained at relatively low temperature and oxygen-isolated circumstance. At such condition, the degree of polymerization is possible to be controlled to remain enough residual monomers to repolymerize and the DMPA can be kept active after the thermo-polymerization. Azobisisobutyronitrile (AIBN)

is chosen as thermo-initiator, because it exhibits less gas generation than other initiators and its pyrolysis temperature is lower than the decomposition temperature of DMPA. Further UV-light illumination leads to extra photo-repolymerization with the help of DMPA. All the reactions are written as



where  $R - R'$  is an organic molecule,  $R \cdot$  and  $R' \cdot$  are radicals. The details of photo-repolymerization are confirmed by measuring the light-induced absorption with the same configuration as that in Ref. [6] and the absorption spectra are shown in Fig. 1. Different from the results in Ref. [6], the reversion points of the change of absorption are not constant any more but dependent on the incident intensity. Compared with the model mentioned in Ref. [6], undoubtedly there are the ground absorption of the pure polymer and the photoinitiator absorption, so more attention should be paid to the third contribution. The reversion point of the change of absorption from positive to negative has an exponential relationship versus the incident intensity, as shown in the inset of Fig. 1, which means that the proportionality constant  $f_R$  is linear to the light intensity. This indicates that the reaction of intermediate products is partly reversible in formula 1 and the reaction equilibrium is influenced by the incident intensity. According to this model, the initiator triggered polymerization of PMMA would act as three processes: chain initiation, chain growth, and chain termination. In DMPA-PMMA, when illuminated with UV-light, the photons are absorbed and decompose the DMPA molecules to free radicals; such radicals trigger the MMA monomer to start a chain polymerization. A quick increase of absorption appears

in chain initiation, since the great amount of photon consumers of DMPA and amount of intermediates are produced, as shown in Fig. 1 when the irradiation is less than about  $5 \text{ J/cm}^2$ . In the chain growth section, the total absorption decreases for the consumption of the DMPA molecules and the intermediate product. The speed of decrease is influenced by the incident intensity for its influence on the reaction equilibrium in the chemical formula 1. When the reaction tends to steady, the chain termination would play a key role until the DMPA molecules and the intermediates are totally consumed. In the photo-repolymerization, the extinction grating is recorded simultaneously with the refractive index grating, and it can be separated from refractive index grating by beam-coupling methods<sup>[11,12]</sup>. Besides measurement of the amplitudes, they also allow us to determine the phase shifts. Usually these methods are based on a fast displacement of the fringe pattern either by moving the sample or by introducing a delay in one of the writing beams<sup>[13–20]</sup>. Our measurement was executed by moving the sample in a traditional two-wave coupling setup. In experiment, the PMMA of 2-mm thickness was fixed on a translation stage which could change the position of the sample along the direction of grating vector. The incident intensity for each beam was  $0.406 \text{ W/cm}^2$ . The crossing angle in air between two recording beams (351 nm from Ar-ion laser) was  $2\theta = 32^\circ$  and the grating spacing  $\Lambda$  was  $636.7 \text{ nm}$ .

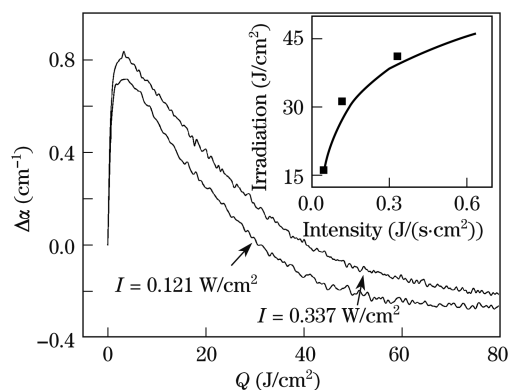


Fig. 1. Change of absorption coefficient versus irradiation  $Q = It$ . The phase transition points from light-induced absorption to light-induced transparency are about  $30 \text{ J/cm}^2$  for  $I = 0.121 \text{ W/cm}^2$  and  $45 \text{ J/cm}^2$  for  $I = 0.337 \text{ W/cm}^2$ , respectively. Inset shows the relationship between irradiation and intensity.

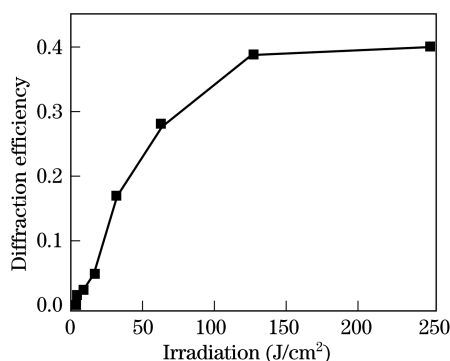


Fig. 2. Diffraction efficiency versus irradiation at  $I = 0.78 \text{ W/cm}^2$ .

During shifting the sample at  $1.2 \mu\text{m/s}$  along the grating vector, the change of both output beams were recorded by two power meters; the diffraction efficiency was measured by blocking one of the incident beams, as shown in Fig. 2.

The method to separate the two kinds of gratings has been carried out based on Kogelnik's beam coupling theory<sup>[11,12,21]</sup>. However, these works were performed under the condition that the diffraction amplitudes  $P$  and  $A$  of the refractive index grating and absorption grating were small. So it was necessary to estimate  $P$  and  $A$  in our experiment to determine whether those calculations were suitable. They are defined by

$$P = \frac{\pi \Delta n d}{\lambda \cos \theta}, \quad A = \frac{\Delta \alpha d}{4 \cos \theta}, \quad (3)$$

where  $\Delta n$  and  $\Delta \alpha$  are the amplitudes of the modulations of the refractive index and absorption, respectively,  $\theta$  is the incident angle, and  $d$  is the grating thickness.

The change of absorption  $\Delta \alpha$  could be gotten from the absorption spectra (Fig. 1) and it has the same order with that mentioned in Ref. [11]. Since the absorption modulation is very small, it is reasonable to predict the order of amplitude of refractive index grating according to Kogelnik's beam coupling theory<sup>[21]</sup>:  $\eta = \sin^2(\pi \Delta n d / \lambda \cos \theta) \exp(-\alpha d / \cos \theta)$ , although it is just suitable for pure refractive index grating. The results show that  $P$  is much bigger than  $A$  and could not be treated as a small value as the former computation any more. So the sum  $I_+(x)$  and the difference  $I_-(x)$  of both interaction beams  $I_1$  and  $I_2$  should be improved with non-simplified  $P$  and written as

$$I_+(x) = I_1 + I_2 = I_0 \exp(-\alpha_0 d / \cos \theta) \times \cos^2 P [2 - 4A \cos(2\pi x / \Lambda + \varphi_a)], \quad (4)$$

$$I_-(x) = I_1 - I_2 = I_0 \exp(-\alpha_0 d / \cos \theta) \times \cos^2 P [-4 \tan P \sin(2\pi x / \Lambda + \varphi_p)], \quad (5)$$

where  $I_0$  is the incident intensity,  $\alpha_0$  is the average absorption constant, and  $\varphi_p$  and  $\varphi_a$  are the spatial dephasings with respect to the light pattern. By fitting the curves of sum and difference of both interaction beams with Eqs. (4) and (5), the dephasings  $\varphi_p$  and  $\varphi_a$  are obtained, as well as the modulations  $\Delta n$  and  $\Delta \alpha$ .

In the experiment, the measurement points were selected at different sections of the photo-polymerization. The diffraction amplitudes ( $A$  and  $P$ ) and the dephasings ( $\varphi_p$  and  $\varphi_a$ ) are shown in Fig. 3–5.

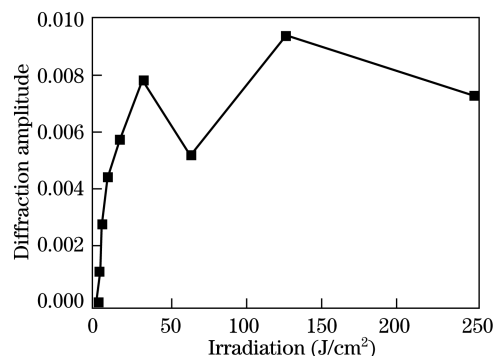


Fig. 3. Diffraction amplitude of the absorption grating versus irradiation at  $I = 0.78 \text{ W/cm}^2$ .

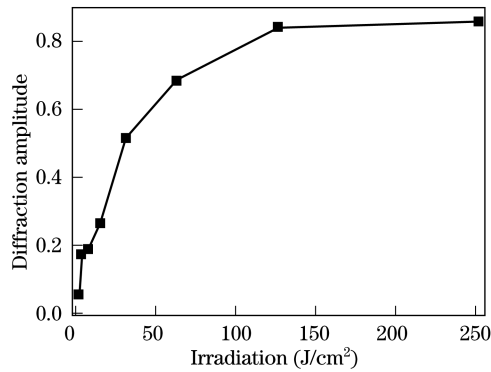


Fig. 4. Diffraction amplitude of the refractive index grating versus irradiation at  $I = 0.78 \text{ W/cm}^2$ .

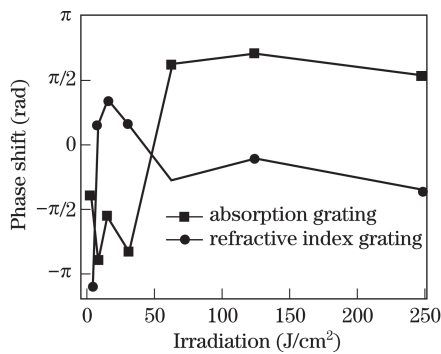


Fig. 5. Phase shift of the absorption grating and the refractive index grating versus irradiation at  $I = 0.78 \text{ W/cm}^2$ .

The absolute diffraction amplitude of absorption grating has a “burning hole” at the irradiation of about  $70 \text{ J/cm}^2$ , which corresponds to the phase transformation point predicted by the light-induced absorption spectrum. This phase transformation indicates a change from light-induced absorption to light-induced transparency and causes a phase reversion of the extinction grating. At the same time, the diffraction amplitude of refractive index grating keeps increasing without any disturbance until the reaction is quasi-stable. Although both of them have contribution to the diffraction efficiency, the refractive index grating affords much more than the extinction grating for that  $P$  is about 100 times bigger than  $A$ , so there is not an obvious interruption of the growth of diffraction efficiency at the phase reversion point of the absorption shown in Fig. 2.

As the holographic gratings are formed based on chemical reaction, the phase shifts would accompany with the polymerization process. At the chain initiation and growth processes, the decomposition of the DMPA as well as the polymerization of the MMA monomers would emit plenty of heat; such heat would result in very acute shrinkage of the sample besides maintaining the further bulk polymerization. So at this time, the phase shift caused by shrinkage is very violent for the acute reaction, as shown in Fig. 5. As the extinction grating mainly originates from the absorption of intermediate products of DMPA, it exists in the illumination area and moves with the shrink of the sample. Nevertheless, the refractive index grating is mainly supported by the difference of density of PMMA at different degrees of polymerization and the polymerization is guided by both the DMPA radicals

and the reaction heat, and it could expand to neighboring area although PMMA is a poor thermo-conductor. As a result, at the chain initiation and growth processes, the phase shift of absorption and phase gratings are decided by both the shrinkage direction of the sample and the polymerization reaction area which is led by the reaction heat conduction direction. So the phase shifts are disordered for acute reaction and random heat conduction.

When the quantity of DMPA is exhausted to a certain level and the diffraction efficiency increases by about 40% as shown in Fig. 2, the reaction rate decreases and less reaction heat is emitted, so the polymerization is approximately limited in the illuminated area and the shrinkage of the sample also becomes weakened. The phases of extinction and phase grating and the phase shift between them become relatively steady for faint polymerization. But for the strain of PMMA under different density, the absorption grating is not local any more but has a small phase shift with respect to the light intensity pattern as well as the refractive index grating. On the contrary, the relative phase shift between the absorption and phase gratings keeps steady at about  $0.9\pi$ . Such phase shifts result in a steady energy exchange between the two coupling beams.

In addition, during the chain termination of PMMA, there might also be acute reaction at some location and the reaction heat sometimes could not be transported away quickly enough, which would result in local superheating; such superheating causes instantaneous shrinkage of gratings and breaks the coupling condition. This leads to additional slight synchronous shifts of the gratings. Such instability of the reaction of PMMA and the shrinkage of the sample might be a key factor to limit the spatial frequencies of the grating to about 10000 lines/mm<sup>[22]</sup>. Fortunately, when PMMA is used as optical device in visible light range, the extinction grating is neglected for the slight change of absorption in this range<sup>[6,10]</sup>. In summary, when recording holographic gratings in DMPA-PMMA, the phase shifts are usually caused by three mechanics: extra thermo-polymerization for heat conduction, shrinkage of the grating for superheating, and the strain for the density difference. Only the strain determines the final phase shifts after photo-repolymerization.

In conclusion, the phase shifts of extinction and refractive index gratings to light pattern have been studied to reveal the mechanism of the energy transfer in two-wave coupling in doped PMMA. The phase shifts of both the extinction and refractive index gratings have contributions to the energy transfer, and the refractive index grating plays the key role especially for visible light. The phase shifts are caused by both the shrinkage and the quasi-steady strain of the sample for both the reaction heat and density difference in local polymerization. Additionally, the instantaneous local superheating also disturbs the stability of the phase shifts slightly. Such shifts and disturbance should be taken into consideration during holographic recording in PMMA and other organic material based on photo-repolymerization.

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