

# Photopolymer Composed of a Photosensitive Polymer Binder Bearing a Chalcone Moiety in the Repeating Unit

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## Abstract

New photopolymers were designed and prepared using the photosensitive polymer binders. Holographic gratings were successfully fabricated in these photopolymer samples by a conventional optical interference method. We also investigated the effect of photocrosslink in the polymer binder on the diffraction behavior of a new photopolymer. The dynamic behavior of the grating formation was monitored by changing exposure intensity in terms of the diffraction efficiency. Particularly, we focused our efforts in observing the variation of diffraction efficiency during a post UV curing process. The surface topographical change of photopolymer layer before and after Vis/UV light exposure was observed by atomic force microscope (AFM). We inscribed the gratings of the glass diffuser on the surface of the photopolymer and investigated their diffusing properties. The diffusers with photopolymer with the main chain polymer binder showed relatively good viewing angle of around  $\pm 30^\circ$ . Two kinds of photopolymer showed similar uniformity of around 47-54%.

**Keywords :** photopolymer, holographic grating, diffraction efficiency, UV exposure, diffuser

## 1. Introduction

Photopolymer (PP) is an attractive holographic material for data storage, other information processing, and display application [1-7]. Therefore, the development of a new photopolymer system has gained much attention in recent years due to its advantages which includes of dry process and ease of storing information. It is widely known that holographic grating can be elaborated easily in the photopolymer film and these gratings can be utilized as a holographic diffuser element in liquid crystal display. A flexible polymeric holographic diffuser is one of the essential components for reducing the production cost of liquid crystal display module.

Generally, a photopolymer consists of polymeric binders, vinyl or acrylic monomers, photoinitiator system, crosslinker, and sensitizing dye [8]. The host polymer binder acts as a supporting matrix containing the other

additive components. The monomers serve as the main species for controlling the index modulation that is induced by optical interference. When PP contains high concentration of low molecular weight compounds in a bulk matrix, we cannot avoid crystallization and phase separation to induce the optical opaqueness of solid film. Although the plasticizing effect from the additives can be expected to facilitate the diffusion of monomers, it is not advantageous for preparing the film and its optical properties.

The basic principle on how to inscribe gratings in photopolymer films had been reported previously [8,9]. First of all, the incident light is absorbed by the photoinitiator to produce free radicals resulting in active radicals and intermediates. Then, the monomers are diminished in the bright regions causing a concentration gradient, which then induces monomer diffusion from the unexposed dark region. Finally, termination of radical propagation occurs through recombination of the radical species. The refractive index modulation arises from the density and compositional differences of molecular chains in the adjacent two regions.

We prepared two kinds of photopolymer systems using the photosensitive binders in this study. Two photosensitive binders contain a chalcone group in the side-chain (PP-1) and main-chain (PP-2) unit, respectively, as shown in Fig. 1.

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The other additive compounds used for preparing the photopolymer film are acrylamide (AA), N,N'-methylenebisacrylamide (BAA), triethanolamine (TEA), and yellow eosin that are already known in the literature.<sup>10-13</sup> The compounds were formulated in tetrahydrofuran (THF)/cyclohexanone (1:0.1 wt. ratio). In our experiment, the thickness of the film sample was adjusted to about 3.3-3.5  $\mu\text{m}$ .

We studied the diffraction properties of the gratings fabricated on our photopolymer films. It was investigated by real-time optical recording. The photopolymerization of acrylamide and photocycloaddition reaction of chalcone-polymer binder were confirmed by UV absorption and infrared spectroscopy. The variation of diffraction efficiency was investigated during UV irradiation in two photopoly-

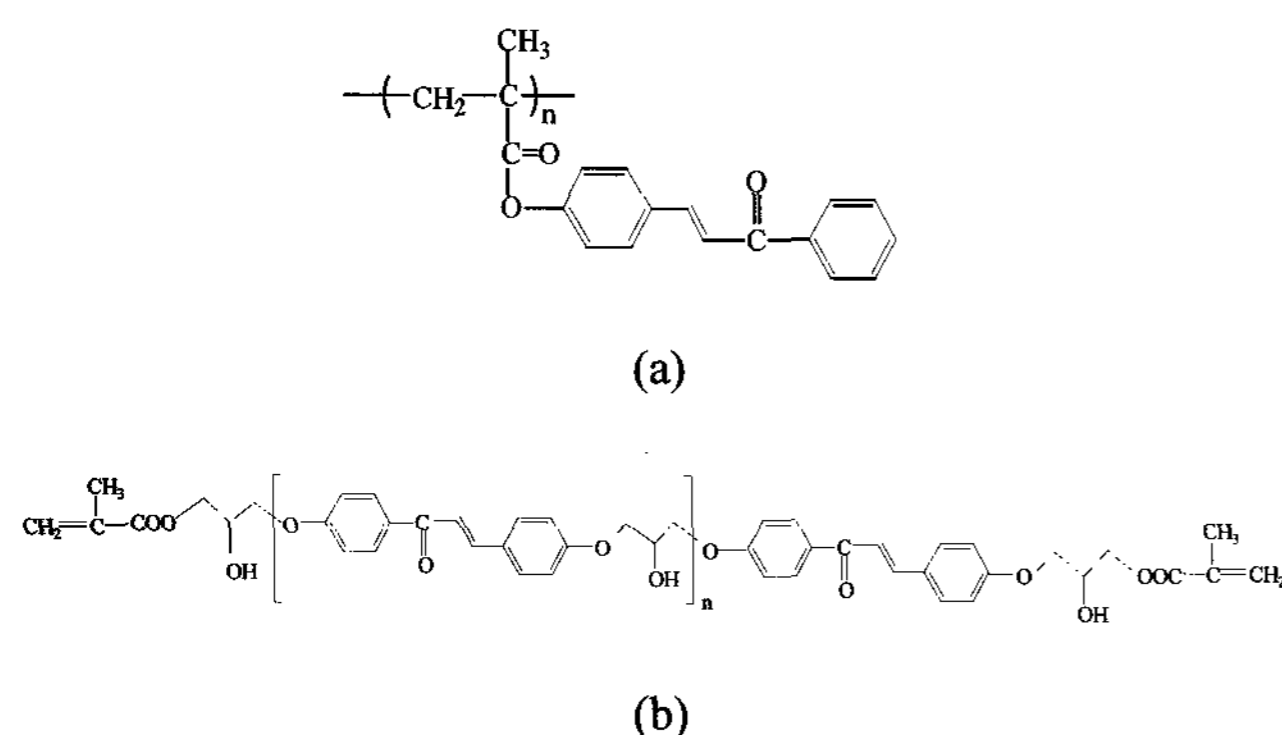
mers. The surface topographical changes of photopolymer film either with or without post UV curing process were also investigated by atomic force microscope.

We also investigated the properties of the holographic diffusing element fabricated with the photopolymers prepared in this study.

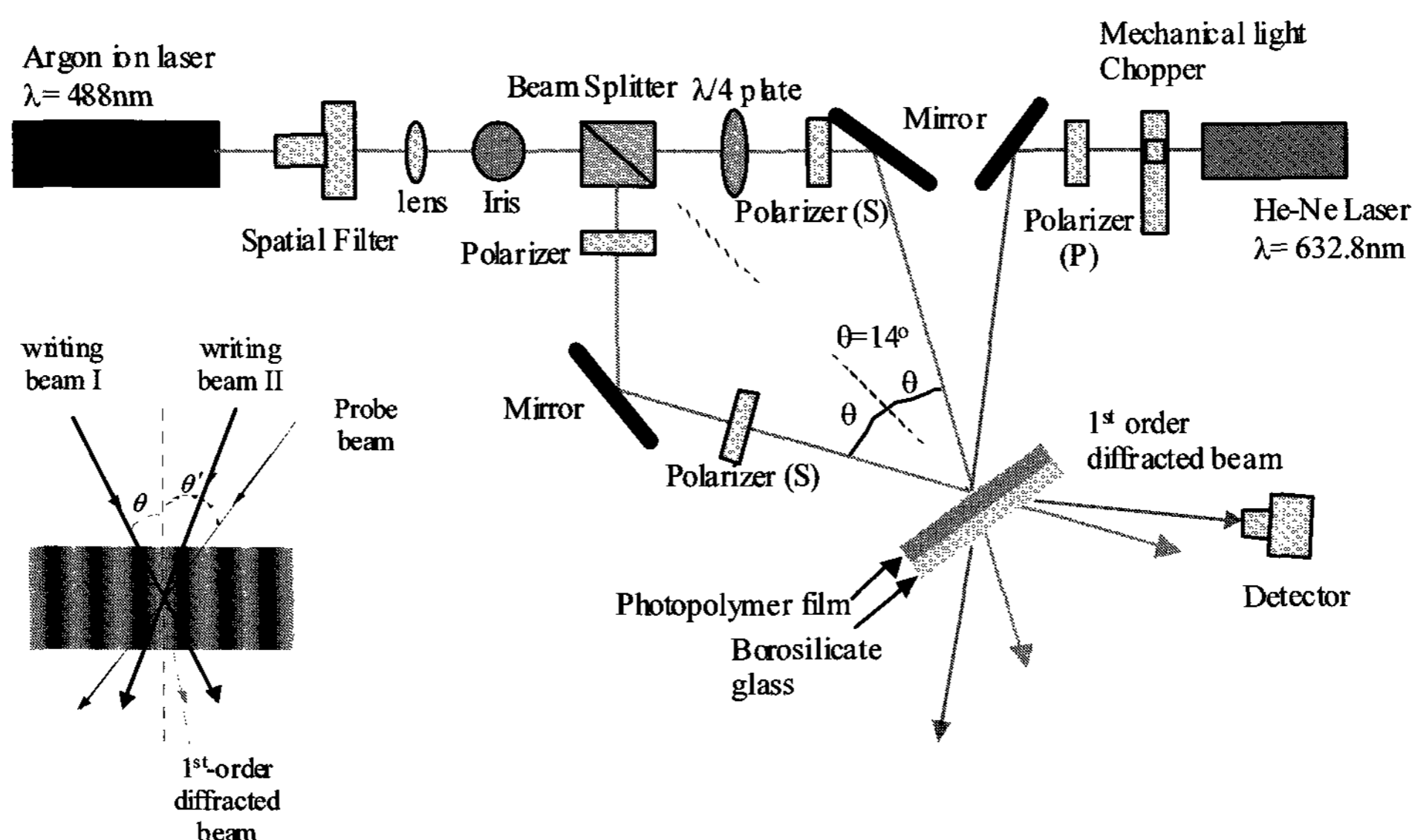
## 2. EXPERIMENT

The schematic diagram for recording the gratings and measuring the first order diffracted light intensity is illustrated in Fig. 2. The Argon ion laser ( $\lambda=488\text{ nm}$ ) was used for recording and the He-Ne laser ( $\lambda=632.8\text{ nm}$ ) was used to probe the recorded grating. Two vertically plane polarized

(s- & s-) 488 nm light beams with equal intensity were obtained by adjusting a quarter wave plate and a polarizers. The basic principle of recording gratings was the optical interference of two excitation beams.<sup>10,11</sup> The intensity pattern consists of bright and dark planes throughout the region of the beam intersection. The angle between the interferential two beams is approximately  $14.6^\circ$ . We can calculate the grating period to be  $1.92\mu\text{m}$  using the equation of  $\Lambda = \lambda / 2 \sin \theta$ . The temporal variation of the first-order diffracted light intensity can be monitored with a probe light from a He-Ne laser (p-polarized  $I=0.5\text{ mW/cm}^2$ ). The probe light was diffracted passing through



**Fig. 1.** The chemical structure of the photosensitive polymer binder. (a) side-chain methacrylate polymer, (b) main-chain polymer endcapped by methacrylate.



**Fig. 2.** Optical setup for measuring the diffracted light intensity.

the gratings with an efficiency  $\eta$  that is defined as the ratio of the 1<sup>st</sup> order diffracted light intensity to the incident light intensity.

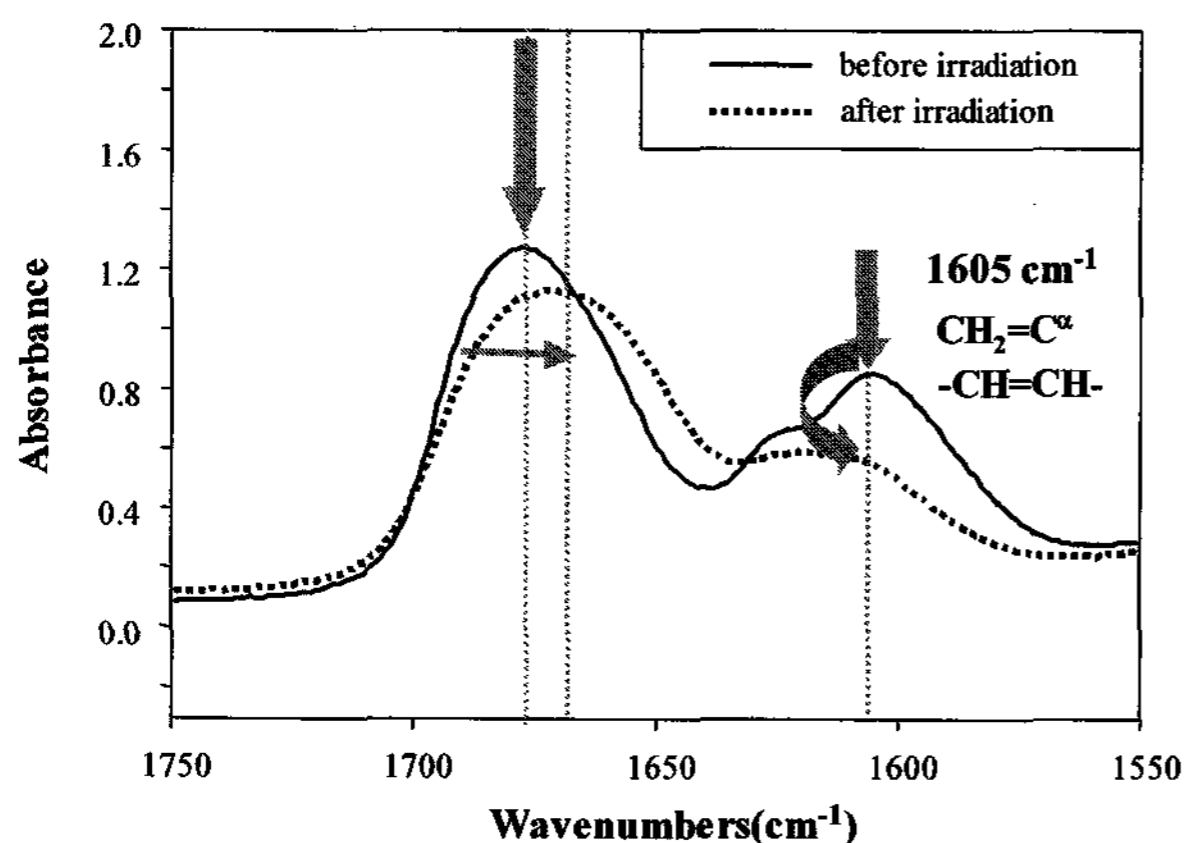
### 3. RESULTS AND DISCUSSION

#### 3.1 Spectroscopic study on the photopolymer films

First, we recorded the infrared spectra of the side-chain photopolymer (PP-1) film before and after visible light irradiation ( $\lambda=488\text{nm}$ ) followed by non-polarized UV light ( $\lambda=365\text{nm}$ ) irradiation. We could confirm the progress of radical polymerization of acrylamide and photocycloaddition of chalcone groups, as shown in Fig. 3. The double bond stretching band of acrylamide at  $1605\text{ cm}^{-1}$  decreased drastically accompanying with the other combination bands. This indicates that acrylamide is polymerized by irradiation of a 488nm visible light. At the same time we can expect that the double bond in chalcone group of the polymer binder will disappear due to cycloaddition reaction.

#### 3.2 Diffraction behavior of the photopolymer consisted of the photosensitive polymer binder

We monitored the diffraction response of the photopolymer under different visible light intensities to estimate light sensitivity. Fig. 4 shows the dynamic behavior of diffraction efficiency under different exposure intensities. The diffraction efficiency increases with increase of the exposure intensity. As the light intensity

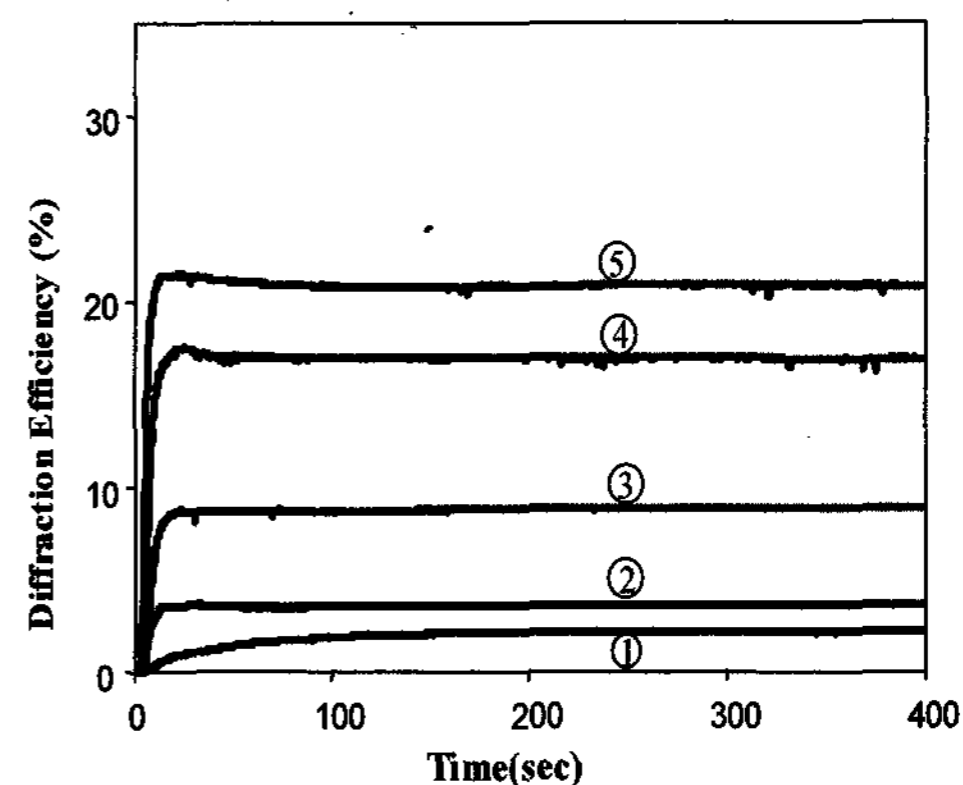


**Fig. 3.** Infrared spectra of the side-chain photopolymer (PP-1) before and after illuminating the excitation light irradiation (1st exposure:  $\lambda=488\text{nm}$ , 2nd exposure:  $\lambda=365\text{nm}$ ).

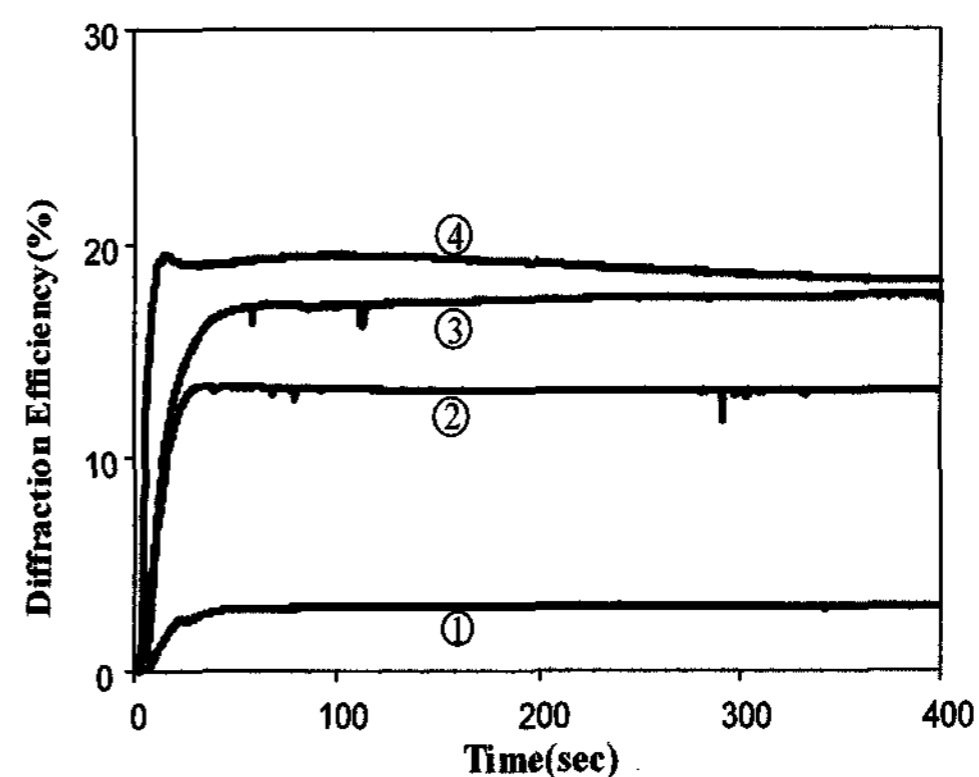
becomes higher, more radical species can be generated to induce more polymerized chains. For that reason, the bright region becomes polymer-rich and the dark region becomes polymer binder-rich.

Assuming that the concentration of the additives, are the same we can express that PP-1 sample will have a higher glass transition temperature than PP-2. Side-chain methacrylate polymer has the glass transition temperature of  $108^\circ\text{C}$  and the  $T_g$  of the main chain polymer cannot be observed at the temperature higher than room temperature.

The degree of polymerization ( $n$ ) of main-chain polymer is around 1-1.3. This was determined by NMR analysis. Therefore, PP-1 sample is more rigid at room temperature. In PP-1. It is more difficult for the monomer to diffuse from dark to bright region under the same intensity



(a)



(b)

**Fig. 4.** Variation of the diffraction efficiency with the change of exposure intensity. (a) PP-1; ①  $28.32\text{ mW/cm}^2$ , ②  $56.64\text{ mW/cm}^2$ , ③  $113.3\text{ mW/cm}^2$ , ④  $169.9\text{ mW/cm}^2$ , ⑤  $566.4\text{ mW/cm}^2$ ; (b) PP-2; ①  $14.16\text{ mW/cm}^2$ , ②  $28.32\text{ mW/cm}^2$ , ③  $56.64\text{ mW/cm}^2$ , ④  $84.96\text{ mW/cm}^2$

of the coupled beams compared to that in PP-2. Therefore, we irradiated a higher intensity of excitation light to achieve the comparable diffraction efficiency of PP-1 samples.

### 3.3 Effect of UV exposure on the diffraction efficiency

Post UV exposure is usually required to induce further polymerization of unreacted residual monomers in the PP films. When the diffracted light intensity through the grating reaches its maximum value and becomes stable, we block the pump beams and begin irradiation of the UV light on the sample (High pressure H<sub>g</sub> lamp). UV exposure continued to induce the polymerization of unreacted residual monomers.

UV light illumination is usually used to fix the grating and illuminate the recessed areas. When the two photopolymer films are irradiated with UV light, the photocycloaddition occurs in the polymer binder, accompanied by the photopolymerization of the unreacted residual monomers; this is different from the properties of other photo-

polymers. As the concentration of unreacted residual monomers is somewhat high, the index modulation ( $\Delta n$ ) decreases, resulting in the decrease of diffraction efficiency for PP-2. (see Fig. 5A) Particularly, in these PPs, the decrease of to be refractive index modulation is expected much larger than the others because we expect two possible reactions of photocrosslink in polymer binder and photopolymerization of the residual monomers in dark region. However, in bright region, the photochemical reactions are difficult to occur since the two polymer chains (e.g. Polymer binder and polyacrylamide) are blended together to separate the same component from each other. Therefore, the distance and the direction between the molecules for photocrosslink and photopolymerization are hardly optimized.

However, in Fig. 5B, no decrement of diffraction efficiency was observed during UV irradiation for PP-1. Sometimes, we can see a slight increase in the diffraction efficiency. This is a very unusual behavior compared to the other photopolymers. In PP-1, one end of the chalcone moiety was tethered to methacrylate backbone. In PP-2, both ends of the chalcone moiety were restricted to move along the main chain. Photocycloaddition in the chalcone groups of PP-1 is likely to occur more quickly and more effectively than that of PP-2. Under UV light illumination to the PP-1 film, photocrosslink occurs faster than the photopolymerization of the residual monomers. Therefore, the refractive indices both in bright and dark region increases, minimizing change of the index modulation. In the bright region, the refractive index increased more than we expected due to the formation of polymer chain network in an interpenetrating way. We can see a slight increase in the index modulation ( $\Delta n$ ) during UV irradiation. However, in PP-2, the photocycloaddition between the main chain units is likely to be much more difficult than that in PP-1. This explain why the photopolymerization of residual monomers and photocycloaddition were so competitive. It is difficult to dimerize chalcone groups due to isolation of the chalcone moieties.

Figs. 6A and 6B show the surface topography of the grating area before and after UV exposure to PP-1 and PP-2 films, respectively. The corresponding exposure intensity for the PP-1 and PP-2 samples is both 114 mW/cm<sup>2</sup>. The depth of refractive index modulation is about 248 nm and the grating periodicity is 2.12 $\mu$ m in PP-1 sample. The modulation depth is about 220 nm and the period of the

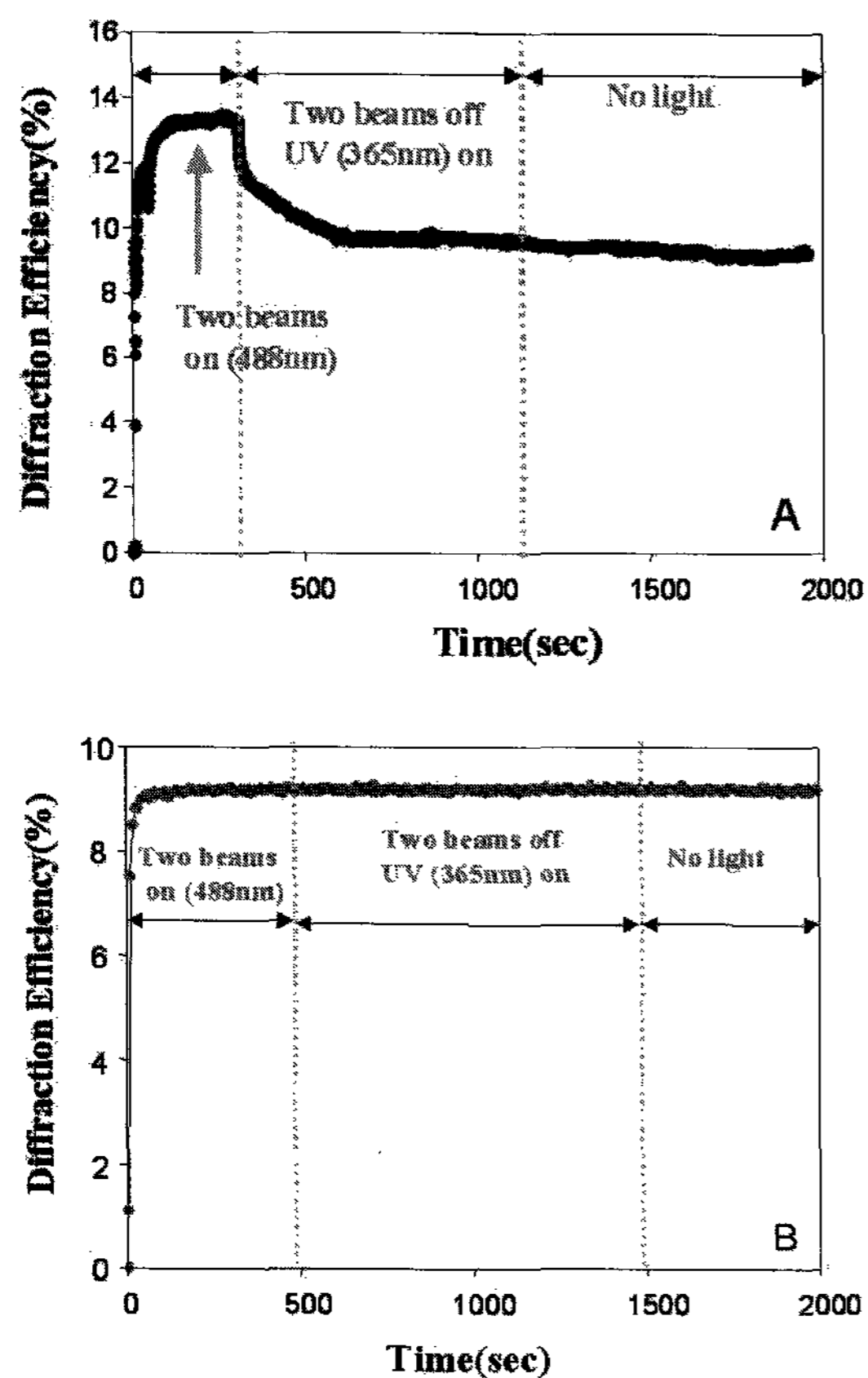
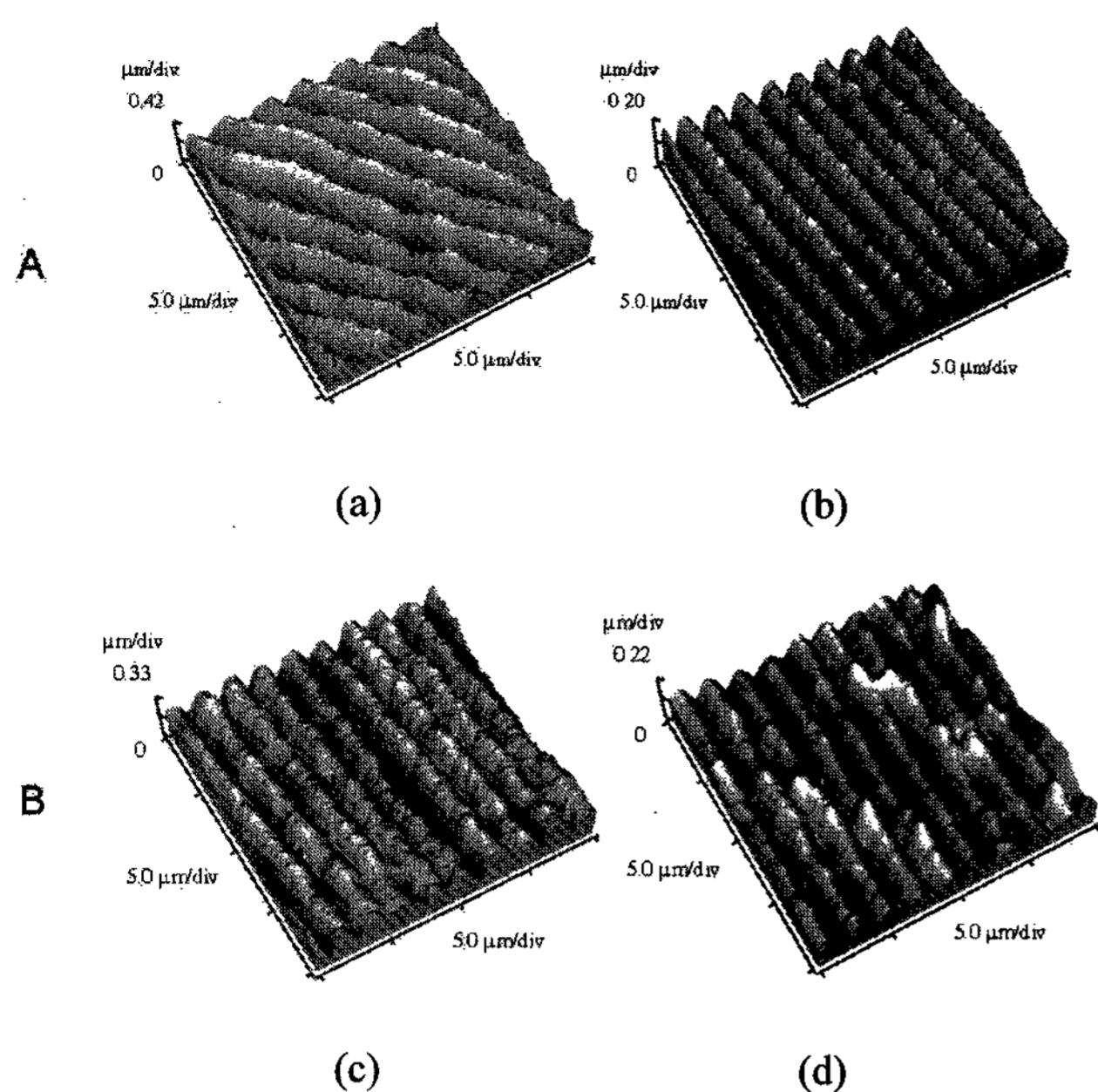


Fig. 5. Variation of the diffraction efficiency during and after UV irradiation. \*Sample : A: PP-2. B: PP-1.

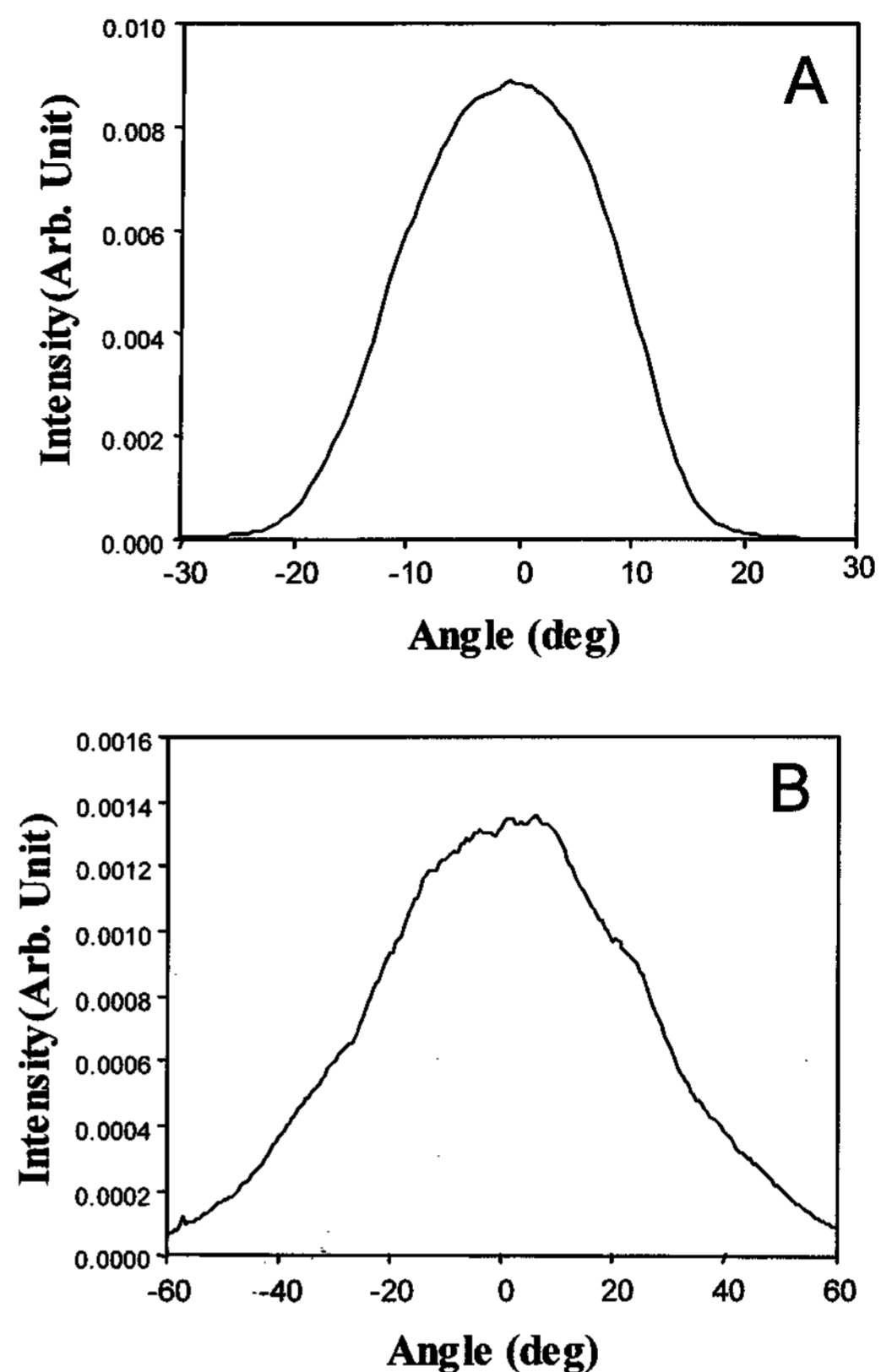


**Fig. 6.** AFM images of the gratings in PP-1(A) and PP-2(B), (a, c) after visible light exposure, (b, d) after Visible and UV exposure.

grating is  $2.12\mu\text{m}$  in PP-2 sample. We compared the surface topography just after visible light irradiation (a or c) and visible/UV light irradiation sequentially (b or d). We could see that the grating resolution and uniformity were greatly improved regardless of volume shrinkage. This is mainly attributed to the fact that the matrix became rigid, resulting from polymerization of the residual monomers and photocrosslinking of the chalcones group in the polymer binder. In PP-1, the periodicity and uniformity of the grating are more clearly resolved than that in PP-2. This may be attributed to difference of the volume shrinkage between two PPs. We plan to further investigate the kinetic behavior of photocrosslink and photopolymerization of the unreacted residual monomers.

### 3.4 Diffuser property fabricated with the photopolymers

We inscribed the surface profile of the glass master diffuser on the surface of the photopolymer. Fig. 7 illustrates the diffusing profiles of the two photopolymers. The viewing angle that we can measure is dependent of the diffusing angle in the master diffuser. When the angle of diffusion is  $60^\circ$  in the master diffuser, the diffusion angle will be in the range of  $-60^\circ$  to  $+60^\circ$  in our optics geometry. In the case the of the diffusers with photopolymer, PP-2 showed relatively promising viewing angle of around  $\pm 30^\circ$ .



**Fig. 7.** Diffracted light intensity as a function of the rotation angle of the diffuser. A: PP-1, B: PP-2.

Using the intensity profile, we could determine the diffusing uniformity comparing the maximum and minimum intensities. PP-1 (A) and PP-2 (B) showed similar uniformity around 47-54%.

Although the performance of the holographic diffuser fabricated in this study is not satisfactory enough for practical application, the diffuser with PP-1 showed better functions than PP-2. We will need to conduct further work to increase the diffraction efficiency and improve the diffuser properties using new sol-gel type photopolymer.

## 4. CONCLUSION

Two kinds of photopolymers were prepared and the holographic gratings were elaborated in film samples by optical interference method. The photosensitive main-chain polymer binder has lower molecular weight in which the monomer can diffuse easily. Then the diffraction efficiency was found to be higher in PP-2 than that of the PP-1 under the same intensity of the laser light. During post UV curing

process, the well-known HRF polymers also showed decrease in the diffraction efficiency. The PP-1 sample prepared in this study showed a unique and unusual property where it did not show any decay in the diffraction efficiency. Post UV-irradiation showed that it improved the grating resolution and the uniformity, which were confirmed by the surface topographical change. The diffuser fabricated with the PPs used in this study showed great potential to be used as a holographic diffuser in real applications.

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