

New Photopolymers Composed of Photoreactive Binder for Holographic Applications (I)

*Dong Hoon Choi, Hanna Yoon, Hyuk Yoon, Geon Joon Lee, Dejun Feng,
Jae Hong Kim, Sang Hyun Paik, [†]Suk-Ho Choi*

College of Environment & Applied Chemistry, [†]College of Electronics & Information,
Materials Research Center for Information Display, Institute of Natural Science,
Kyung Hee University, Yongin 449-701, Korea

ABSTRACT

New photopolymers were designed and prepared using the photosensitive polymer binders. The photochemical reaction of the photosensitive polymer binder was studied by virtue of UV absorption and infrared spectroscopy. The holographic gratings were successfully fabricated in these photopolymer film samples by conventional optical interference method. We also investigated the effect of photocrosslink in the polymer binder on the diffraction behavior of the photopolymer. The dynamic behaviors of the grating formation were studied with the change of exposure intensity in terms of the diffraction efficiency. Particularly, we focused our efforts to observe the variation of the diffraction efficiency during post UV curing process.

1. INTRODUCTION

Photopolymer (PP) was an attractive holographic material for data storage, other information processing and display application etc [1-7]. Therefore, development of new photopolymer system had gained much attention in recent years due to the advantages of dry process, ease of storing information etc. It was widely known that a holographic grating could be elaborated easily in the photopolymer film.

Generally, the photopolymer typically consists of polymeric binders, vinyl or acrylic monomers, photoinitiator system, crosslinker, and sensitizing dye [8,9]. The host polymer binder acts as a supporting matrix containing the other additive components. The monomers serve as the governing species to control the index modulation, induced by optical interference. When the PP contains high concentration of low molecular weight compounds

in the matrix, we cannot avoid crystallization and phase separation to induce optical opaqueness of the film. Although the plasticizing effect from those additives can be expected to facilitate the diffusion of the monomer, it is not advantageous for the film forming and the optical properties.

We prepared two kinds of photopolymer systems using the photosensitive binders in this study. These two photosensitive binders have a chalcone group in the side-chain (PP-1) and main-chain (PP-2), respectively, as shown in Figure. 1. The other additive compounds used for the preparation of the photopolymer film samples were acrylamide (AA), N,N'-methylenebisacrylamide (BAA), triethanol amine (TEA), and yellow eosin that are already known in the literature [10-13]. The compounds were formulated in tetrahydrofuran (THF) /cyclohexanone (1:0.1 wt. ratio). In our experiment, the thickness of the film sample was adjusted about 3.3-3.5 μm .

We studied the diffraction properties of the gratings fabricated in our photopolymer systems, which were 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 difference of the variation of the diffraction efficiency was investigated during UV irradiation in two photopolymers.

2. EXPERIMENT

The Argon laser ($\lambda=488, 514$ nm) was used in recording and the He-Ne laser ($\lambda=632.8$ 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 the quarter wave plate and the polarizers appropriately, which was used for fabricating the holographic grating. The basic principle of recording gratings was based on optical interference [10,11]. The angle between the interferential two beams is approximately 14.6° , so we can calculate the grating period of $1.92 \mu\text{m}$ theoretically determined by the relationship 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 through the gratings with an efficiency η that was defined as the ratio of the 1st order diffracted light intensity to the incident light intensity.

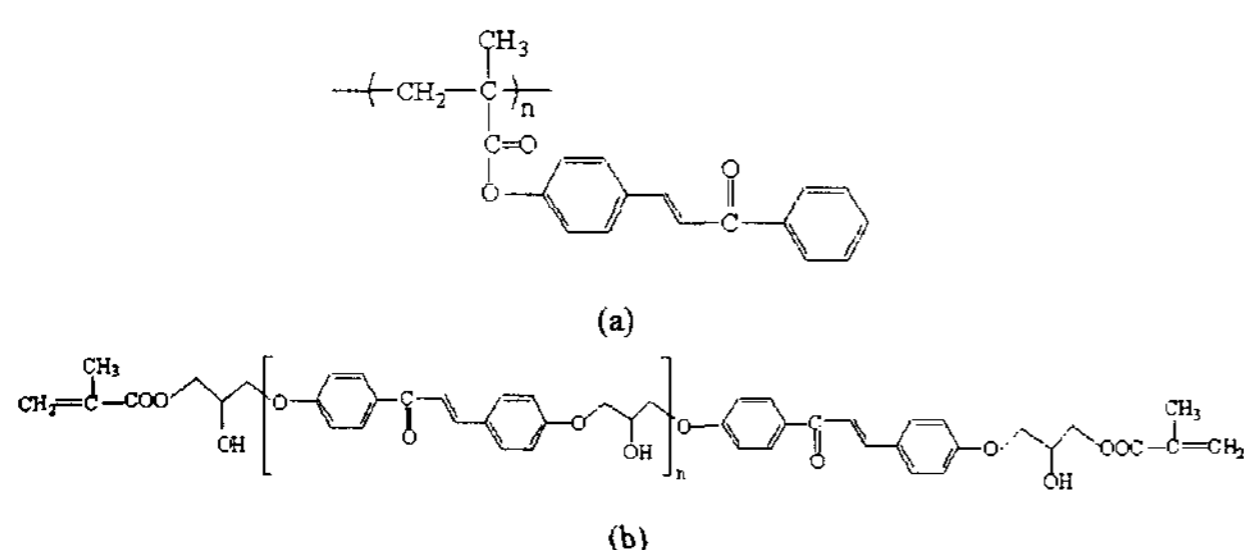


Figure 1. The chemical structure of the photosensitive polymer binder. (a) side-chain methacrylate polymer, (b) main-chain polymer endcapped by dimethacrylate.

3. Results

3.1 Spectroscopic study on the photopolymer films

Firstly, we recorded the infrared spectra of the side-chain photopolymer (PP-1) film sample before and after visible light irradiation ($\lambda=488\text{nm}$) followed by non-polarized UV light ($\lambda=365\text{nm}$) irradiation in order to confirm the progress of radical polymerization of acrylamide and photo-cycloaddition of the chalcone groups, as shown in Figure 2. The double bond stretching band of acrylamide at 1605 cm^{-1} decreased significantly accompanying with the other combination bands. This indicated that acrylamide underwent the polymerization by irradiation of the visible light. At the same time we could expect that the double bond in chalcone group of the polymer binder

disappeared due to cycloaddition reaction. During UV irradiation, the absorbance at 313 nm is decreasing with the irradiation time. Therefore, both photopolymerization and photocrosslink were confirmed by spectroscopic results.

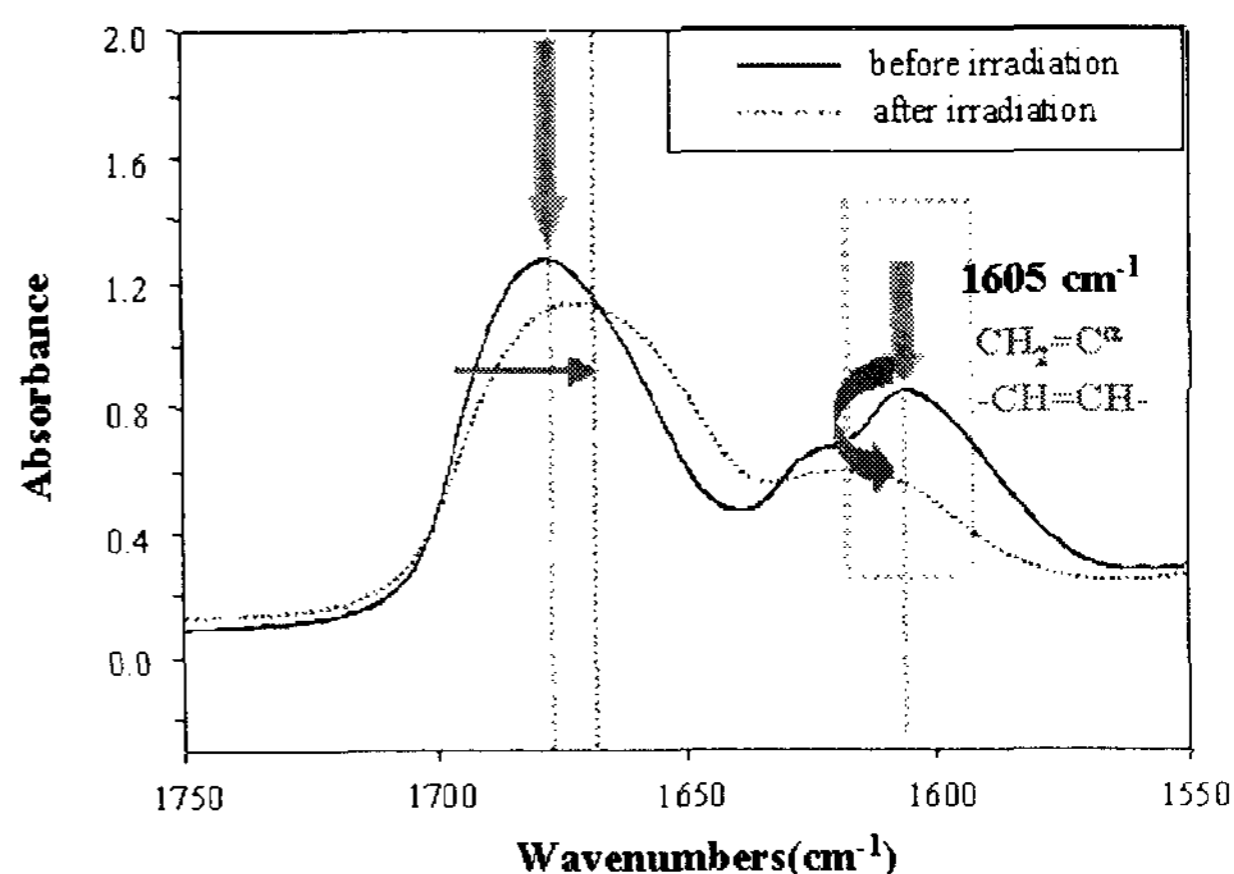


Figure 2. Infrared spectra of the side-chain photopolymer (PP-1) before and after excitation light irradiation (1st exposure: $\lambda=488\text{nm}$, 2nd exposure: $\lambda=365\text{nm}$).

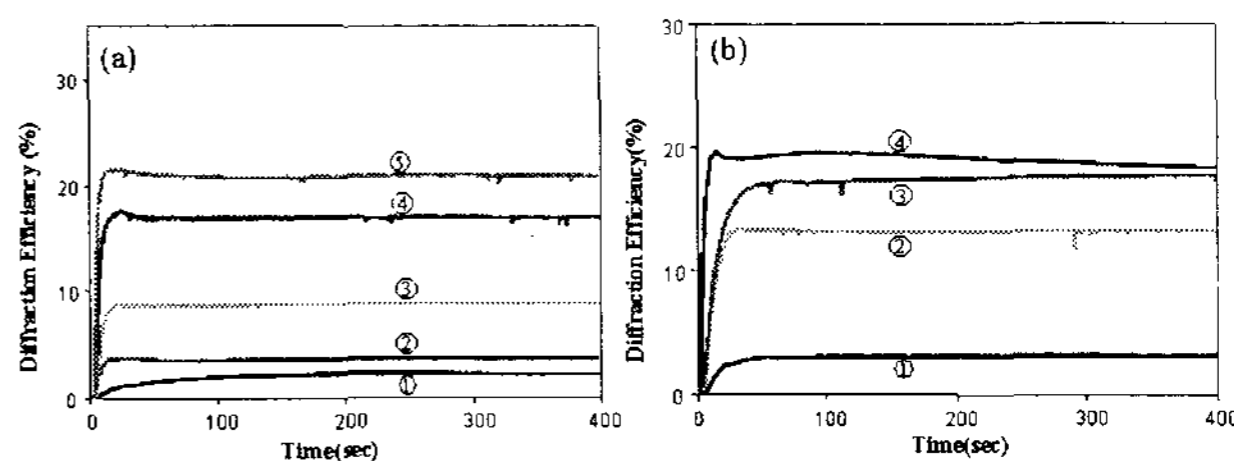


Figure 3. Variation of the diffraction efficiency with the change of the exposure intensity.

(a) PP-1; ① 28.32 mW/cm^2 , ② 56.64 mW/cm^2 , ③ 113.3 mW/cm^2 , ④ 169.9 mW/cm^2 , ⑤ 566.4 mW/cm^2 ; (b) PP-2; ① 14.16 mW/cm^2 , ② 28.32 mW/cm^2 , ③ 56.64 mW/cm^2 , ④ 84.96 mW/cm^2

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

We studied the diffraction response of the photopolymer grating under different light intensities to estimate the light sensitivity.

Figure 3 shows the dynamic behavior of the diffraction efficiency under different exposure intensities. It is clear that the diffraction efficiency will increase with the increase of the exposure intensity. In both PPs, the diffraction efficiency

reached to around 20-22%. However, under higher light intensity, we could achieve it around 60-70%.

3.3 Effect of UV exposure on the diffraction efficiency

In most cases of PP, post UV exposure will be required to induce further polymerization of the unreacted residual monomer in overall regions of the film samples. When the diffracted light intensity through the grating reaches its maximum value and becomes stable, we block the pump beams and start to irradiate the UV light on the sample (High pressure H_g lamp). UV exposure kept for 0.5 hr to induce the polymerization of unreacted residual monomers. UV irradiation is usually used to fix the grating and expose the recessed areas that are not exposed to laser light. When the two photopolymer samples were irradiated with UV light, the photocycloaddition can occur in the polymer binder accompanying with photopolymerization of the unreacted residual monomers, which is dissimilar to the other photopolymers.

In this case, when the concentration of the unreacted residual monomer is somewhat high, the index modulation (Δn) decreases, resulting in decrease of the diffraction efficiency too, as shown in Figure 4(a) for PP-2. Particularly, in these PPs, the decrement of the refractive index modulation will be expected to be much larger than the others because we can expect the two possible reactions of photocrosslink in polymer binder and photopolymerization of the residual monomers in dark region. However, in the bright region, the photochemical reactions were hard to occur since the two polymer chains (eg. Polymer binder and polyacrylamide) were blend together to make the same component apart each other. Therefore, the distance and the direction between the molecules for the photocrosslink and photopolymerization will be hardly satisfied. Additionally, the volume shrinkage from two photochemical reactions will decrease the film thickness to lower the diffraction efficiency.

However, in Figure 4(b), we could not observe any decrement of the diffraction efficiency during UV irradiation for PP-1. Sometimes, we could observe slight increase of the diffraction efficiency. This is very unusual behavior compared to the other photopolymers. We conjecture the following reason

for explaining this unusual behavior. In PP-1, one end of chalcone moiety was tethered to the methacrylate backbone. In PP-2, both ends of the chalcone moiety were restricted along the main chain. Photocycloaddition of the chalcone groups

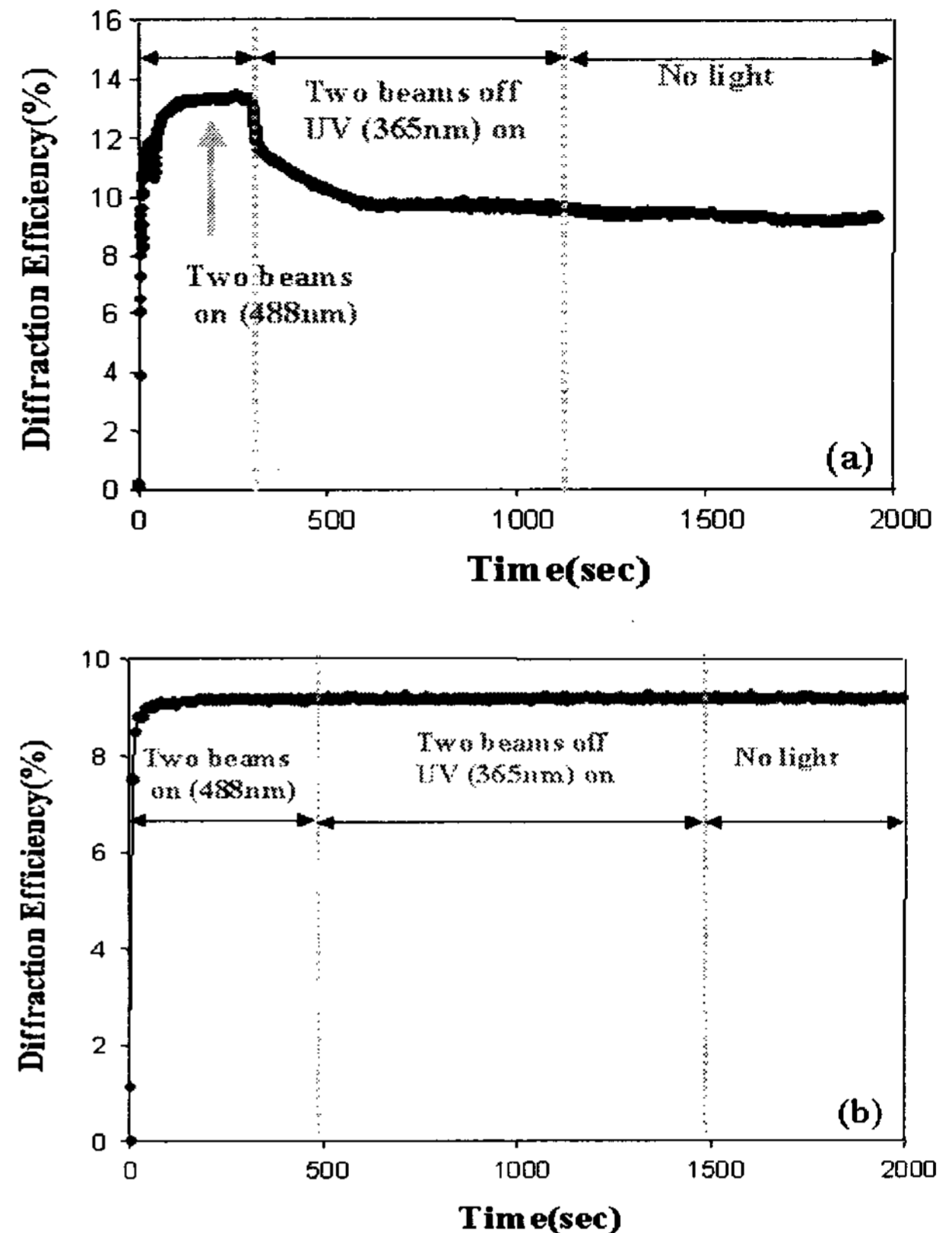


Figure 4. Variation of the diffraction efficiency during and after UV irradiation. *Sample : (a) main-chain photopolymer PP-2, (b) side-chain photopolymer PP-1.

in PP-1 is likely to occur much faster and more effectively than that in PP-2. In our respect, in PP-1, under UV irradiation, the photocrosslink proceed faster than the photopolymerization of the residual monomers do. Therefore, the refractive index in bright and dark region all increased so that the index modulation cannot be changed. Sometimes, in bright region, the refractive index increased more than we expected due to the formation of polymer chain network in an interpenetrating way. In that case, we can observe the slight increase of index modulation during UV irradiation. However, in PP-2, the photocycloaddition between the main chain unit is likely

to be much more difficult than that in PP-1. Therefore, the photopolymerization of the residual monomers and photocycloaddition were so competitive and then the chalcone groups are scarcely dimerized resulting from isolation of the chalcone moieties mutually. This behavior in PP-2 is similar to that of the other conventional photopolymers.

We are making some efforts to investigate the kinetic behavior of photocrosslink and photopolymerization of the unreacted residual monomers.

4. CONCLUSION

Two kinds of photopolymers were studied and the holographic gratings were elaborated in film samples by the 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 achieved to be higher in PP-2 than that of the PP-1 under an identical intensity of the laser light. During post UV curing process, the well-known photopolymers also showed the decrement of the diffraction efficiency. The PP-1 sample prepared in this study showed unique and unusual property to show no decay of the diffraction efficiency.

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