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Diffraction Behaviors of New Photopolymers and their Diffuser Properties

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Abstract

Photopolymers are quite promising candidates for holographic data storage and diffusers because of their high sensitivity and high refractive index modulation. New photopolymers were prepared using the cellulose ester binder bearing different kinds of monomer. The holographic gratings were elaborated successfully in these photopolymer samples by conventional optical interference method. We investigated the dynamic behavior of the diffraction efficiency and the effect of the functionality of the monomer doped into the polymer binder. Triacrylate monomer doped photopolymer showed the highest diffraction efficiency of around 80-90 %, even under low intensity of writing beam (I=2 mW/cm^2). We inscribed the gratings of the glass diffuser on the surface of the photopolymer and investigated their diffusion properties.

Keywords : photopolymer, diffraction efficiency, diffuser, viewing angle

1. Introduction

Photopolymers (PPs) are promising materials systems of organic molecules that are based on photoinitiated polymerization for recording volume holograms. They are very attractive as holographic materials for holographic data storage and display application, etc [1-6]. Therefore, great attention has been drawn to new photopolymer system in recent years due to the advantages of dry process, ease of storing information, etc. It is widely known that holographic gratings can be elaborated easily in the photopolymer film. Characteristics such as a good light sensitivity, large dynamic range, good optical quality, and relatively low cost make photopolymers one of the most promising materials to be used in line shaped diffuser and write-once, read many (WORM) holographic data storage applications [1-6].

Numerous photopolymerizable material systems for holographic storage applications have been developed since the photopolymer was first discoverd in 1969 [6]. The storage medium must have low absorption at the recording wavelength to achieve uniform recording for each thickness of the material. In addition high concentration of low molecular species must be contained in the photopolymer for holographic grating formation and the doped monomers must undergo fast and complete photoinduced polymerization followed by diffusion of the doped monomer in the photopolymer. Generally, the photopolymer consists of polymer binders, vinyl or acrylic monomers, photoinitiator system, crosslinker, and sensitizing dye [7, 8]. The host polymer binder acts as a supporting matrix containing the other low molar mass components. The monomers serve as another important species that govern the index modulation induced by optical interference.

The basic principle for elaborating gratings in photopolymer films had been reported previously [9, 10]. First of all, the incident light is absorbed by the photoinitiator system to produce active radicals. Then, monomers become polymerized in the bright region, causing a concentration gradient, to occur which then induces monomer diffusion from the unexposed dark region. Finally, propagation is terminated by the recombination of the radical species or chain transfer to the polymer binder or monomer. The refractive index modulation results from the compositional difference of the molecular chain in the adjacent two regions.

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Most polymer binders behave as a supporting matrix for other additives, and after visible light irradiation, the polymer binder and newly formed polymer are blended simply through physical interaction such as through hydrogen bond, Van der Waals interaction. The diffraction property is dependent of the index modulation which is affected by the molecular weight and the degree of crosslinking of the newly formed polymer.

In this study, we employed three different monomers and introduced them into the cellulose ester binder. All the monomers belong to the class of acrylate compound. Di-, and triacrylate monomers were employed to prepare the PP formula. Since we were interested in the effect of the monomeric species on the diffraction property, we studied the dynamic behaviors of the diffraction property according to the change in the monomeric species by perfoming real time monitoring systematically. The polymer binder and the monomers used herein are illustrated in Fig. 1. The other additive compounds used for the preparation of the photopolymer film samples were triethanolamine (TEA) and 2',4',5',7'-tetrabromofluorescein (TBF) which are have already been reported in previous literatures [11-13]. The variation in the diffraction efficiency was investigated at room temperature for three photopolymers. We also investigated the properties of the holographic diffusing element fabricated with the photopolymers prepared in this study.

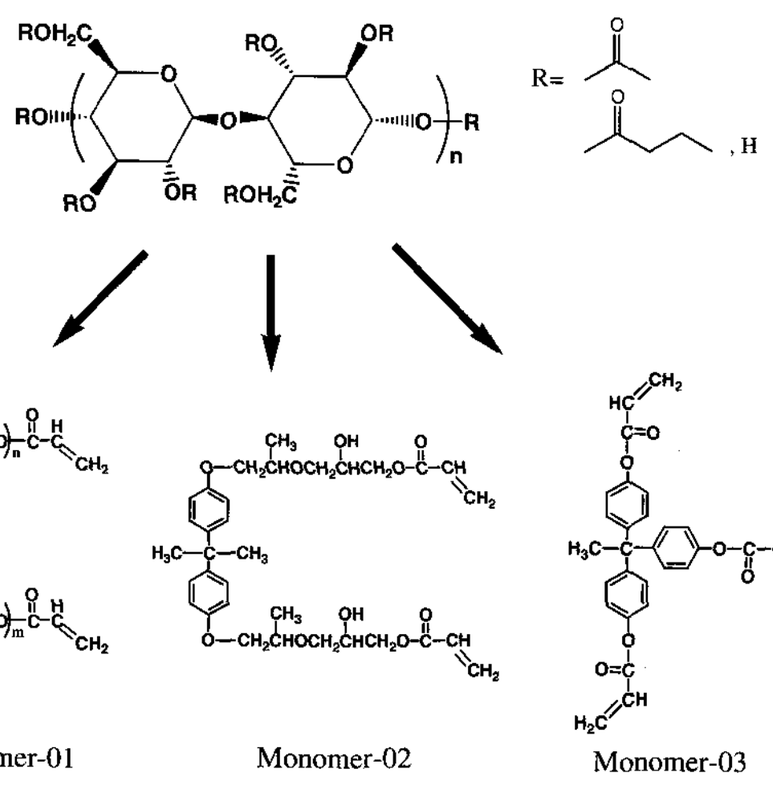

Fig. 1. Chemical structures of the polymer binder and the monomers. (Monomer-01: bisphenol A ethoxylate diacrylate, Monomer-02: bisphenol A propoxylate glycerolate diacrylate, Monomer-03: acrylic acid 4-[1, 1-bis-(4-acryloxy-phenyl)-1-methyl-ethyl]-phenyl ester).

2. Experiments

2.1 Preparation of the photopolymers

The compositions of the photopolymers are shown in Table 1. The cellulose acetate butyrate (Mw 30000, 2 wt% Acetyl, 52 wt% Butyryl) was selected as a polymer binder. Monomers (0.29-0.7 M) were introduced into the polymer binder in the presence of triethanolamine (0.9 M) and 2',4',5',7'-tetrabromofluorescein (2.1×10^{-7} M). The difference in the diacrylate monomers (Monomer-01, Monomer-02) demonstrates that hydroxy group exists in the monomer. Also, we prepared triacrylate monomer (Monomer-03) to change the number of monomer functionality for polymerization. The compounds were formulated in tetrahydrofuran (THF) and after degassing the solution (conc. 16 wt%) for 24 hr, it was cast on the borosilicate glass. In our experiment, the thickness of the PP film sample was adjusted about 140 μm and measured by Alpha Step P10.

Table 1. Concentration of monomer and determined parameters of three photopolymers

	Monomer (M)	Thickness (μm)	Max . Diffraction Efficiency (%)	Photosensitivity (mJ/cm^2)	Uniformity (%)	Viewing Angle (°)
PP-01	7.0×10^{-2}	140	12	280	83	±10
PP-02	3.3×10^{-2}	140	37	180	70	±7
PP-03	2.9×10^{-2}	140	78	220	37	±30

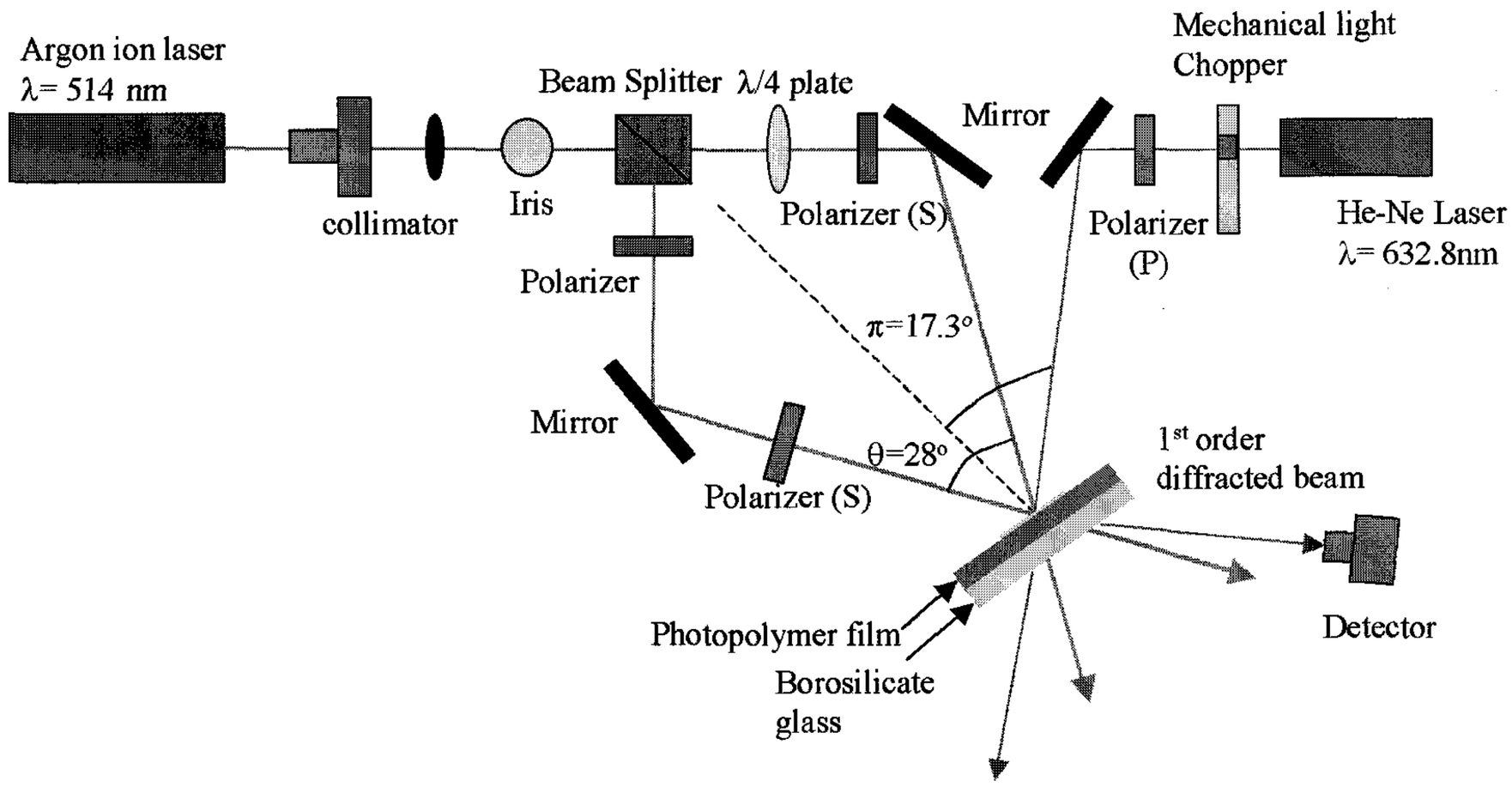

Fig. 2. Optical setup for measuring the diffracted light intensity of the photopolymer.

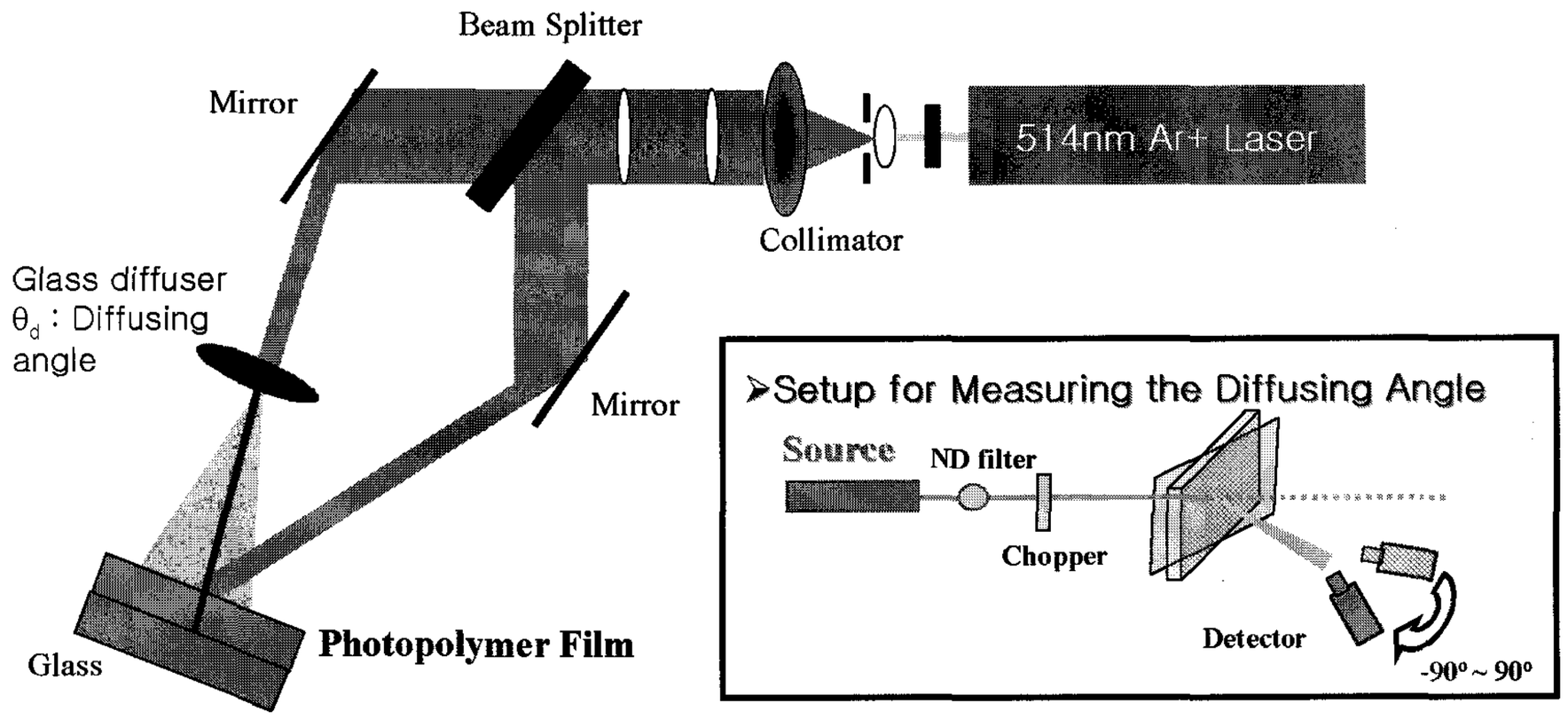

Fig. 3. Optic set up for fabricating diffusing element and measuring the diffusing angle.

2.2 Measurement of diffraction efficiency and fabrication of the diffusing element

The schematic diagram for the recording of the gratings and measurement, the first-order diffracted light intensity was illustrated in Fig. 2 Argon ion laser (λ=514 nm) was used for recording and He-Ne laser (λ=632.8 nm) was used to probe the recorded grating. The beam was expanded using a microscope objective and spatial filter. The writing beam was passed through spatial filter to produce planar collimated light. Two vertically plane polarized (s- & s-) light beams of equal intensity were obtained by appropriately adjusting the quarter wave plate and the polarizers and fabricating the holographic grating. The basic principle behind the recording gratings is based on optical interference. The intensity pattern consisted of bright and dark planes throughout the region of the intersection. This offers an refractive index grating in the material through diffusion and photopolymerization of the monomer. The angle between the interferential two beams was set to be 28°. Temporal variation of the 1st order diffracted light intensity could be monitored with a probe light from a He-Ne laser (p-polarized I= 0.5 mW/cm^2). The

incident angle for the He-Ne laser beam to the sample was set to be 17.3°. 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.

In order to fabricate the diffuser, we employed a glass diffuser (Newport 20DKIT-C2, 10°) to inscribe the grating on the surface of the photopolymers after expanding and focusing the object beam on the glass diffuser. We measured the profile of the diffracted light intensity the rotation angle for investigating the uniformity, diffusing angle etc. (See Fig. 3)

3. Results and Discussion

The polymer binder plays an important role in imposing the physical properties of the photopolymer, such as its rigidity, environmental stability, volume change upon light exposure and moderate thickness. For fabricating the holographic diffuser, the binder must have good film forming property and good thermal-/ photostability. There factors also affects the diffusion property of the doped monomers, including photoinduced refractive index change. Monomer is another crucial component in the development of the higher index modulation, along with the binder. During polymerization, the variation of the molecular weight and crosslink in the polymer binder can be achieved by controlling the light dose. In this work, we used two diacrylate monomers such as bisphenol A ethoxylate diacrylate, bisphenol A propoxylate glycerolate diacrylate, and acrylic acid 4-[1,1-bis-(4-acryloxy-phenyl)-1-methyl-ethyl]-phenyl ester with the structure and the number of functionality (Fig. 1). We investigated the effect of monomeric species on the diffraction property and diffuser property.

3.1 Diffraction behaviors of the photopolymers with different monomers

We studied the diffraction behaviors of the photopolymers under different intensities of the writing beam. Fig. 4 shows the dynamic behavior of the diffraction efficiency in PP-01 series bearing bisphenol A ethoxylate diacrylate under irradiation of excitation light (I=1, 3, and 6 mW/cm^2). It is clear that the diffraction efficiency increases with the increase of the intensity of light. As the light intensity is higher under the fixed concentration of

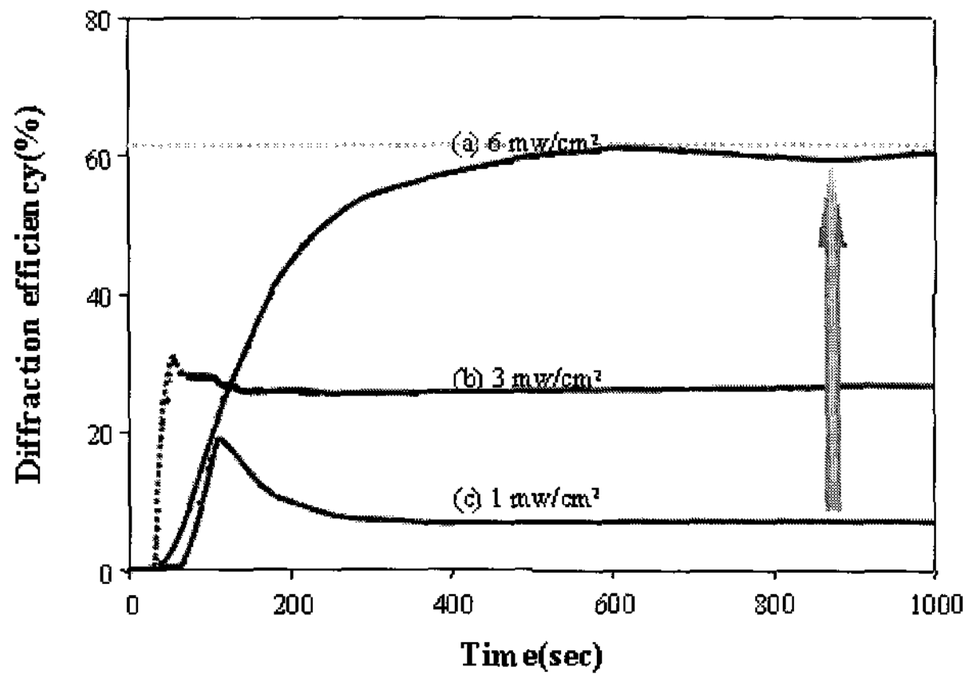

Fig. 4. Variation of the diffraction efficiency of PP-01 with the intensity of the writing beam. (a) 6 mW/cm^2, (b) 3 mW/cm^2, (c) 1 mW/cm^2.

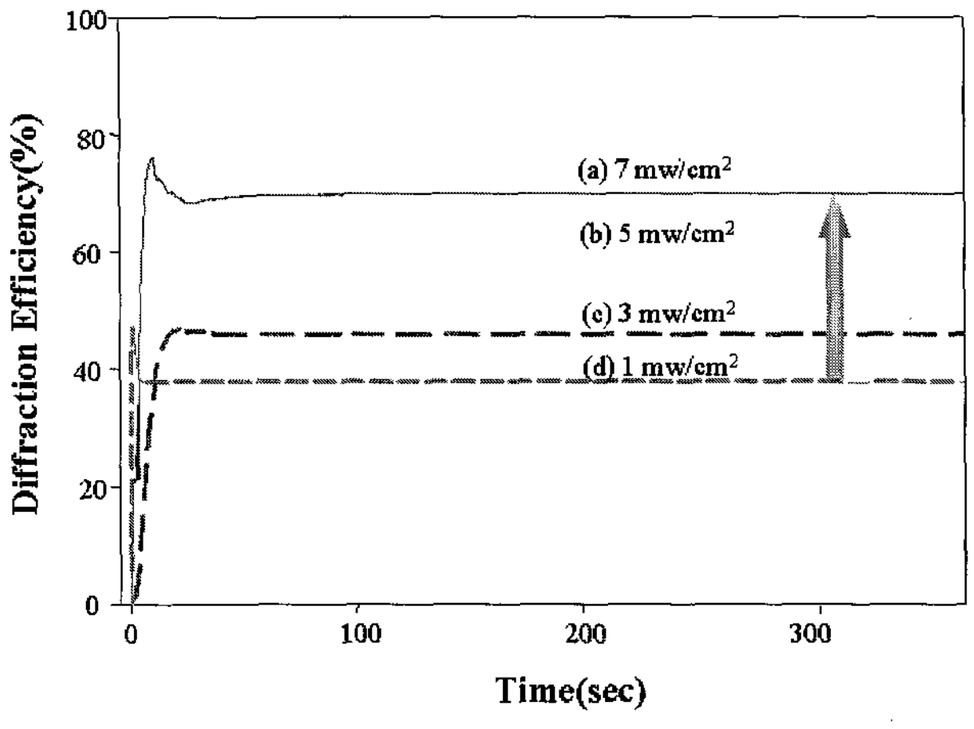

Fig. 5. Variation of the diffraction efficiency of PP-01 with the intensity of the writing beam. (a) 7 mW/cm^2, (b) 5 mW/cm^2, (c) 3 mW/cm^2, (c) 1 mW/cm^2.

initiating species, we observed that more initiating species were generated to propagate the polymerization accompanying with generation of macro radicals. Maximum diffraction efficiency could be achieved around 60 %, which is relatively high. As a result the constructive region were found to become more polymer-rich and the destructive region becomes more polymer binder-rich. As shown in Fig. 5, we could observe similar trend of rising behavior of the diffraction efficiency in the PP-02. However, at the same time, we could observe higher rate of the diffraction efficiency at the smaller molar concentration of monomer compared to that of previous experiment (e.g. PP-01). The diffraction efficiency also showed a slight increment even

though the molar concentration of the doped monomer was lower due to the larger size of the monomer. The average molecular weight of monomer-01 should be 514. Particularly, the initial rising behavior showed much faster and stabilized within a very short time. Among the three monomers used herein, only monomer-02 contained two hydroxy groups along the molecules.

In the photopolymer with cellulose ester polymer binder, termination of polymerization could be induced by radical recombination and chain transfer reaction to the binder generally. However, in PP-02, another kind of chain transfer reaction occurred between the monomer and macroradicals. Therefore, a short segment of the polymer chain in PP-02 was formed, causing polymerization to be terminated at a faster rate than that in PP-01. This explains the faster rate of rising behavior of the diffraction efficiency and faster stabilization in PP-02.

In most rising curves, we could observe initial ransient behavior to show a different increasing rate. Particularly, at the lower concentration of the monomer, secondorder kinetic behavior can be considered. This implies that in the initial period of illumination, the existing monomers in the constructive region polymerized to increase the refractive index in the localized region before the monomers started to diffuse into the constructive region. If the concentration gradient along the region was not so high, the first order rate of diffusion would have been relatively small.

In Fig. 6, we investigated the PP-03 photopolymers containing triacrylate monomer under the relatively lower intensities of the writing beam. This triacrylate compound was synthesized to obtain as a white powder, which is different from the previous two viscous liquid monomers such as diacrylate. We observed that it dissolved well in the solvent mixture of THF, showing good miscibility in the polymer solution. Although 0.29 M of the monomer was blended with polymer binder and other additives, we could still fabricate very transparent polymer films optically. In this case, the diffraction efficiency was observed to be higher than 80 %. When the irradiation of two excitation beams was prolonged we could achieve a diffraction efficiency of 95 %. This means that most of the fundamental probe beam was converted to the 1-st order diffracted light. Compared to the previous two photopolymers (PP-01, PP-02), the holographic performance of the photopolymer was greatly improved by using the triacrylate monomers. Three double bonds in the monomer bonded strongly with the core molecule without aggregation and was found to propagate easily in a 3-dimensional way to form the network structure having a number of crosslink.

Comparing the dynamic behaviors and value of the diffraction efficiency in the PP-01, PP-02, and PP-03, it is clear that the PP-03s show higher diffraction efficiency. From this, it can be assumed that the kind of monomer has significant effect on the diffraction behavior. The large sized triacrylate monomer can effectively induce chain

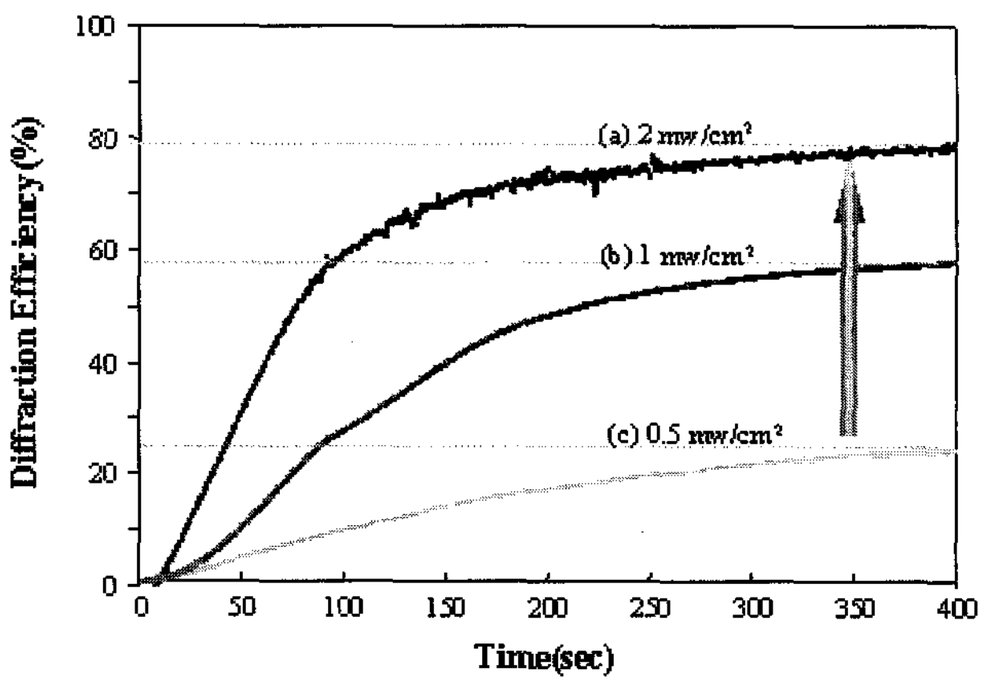

Fig. 6. Variation of the diffraction efficiency of PP-01 with the intensity of the writing beam. (a) 2 mW/cm^2, (b) 1 mW/cm^2, (c) 0.5 mW/cm^2.

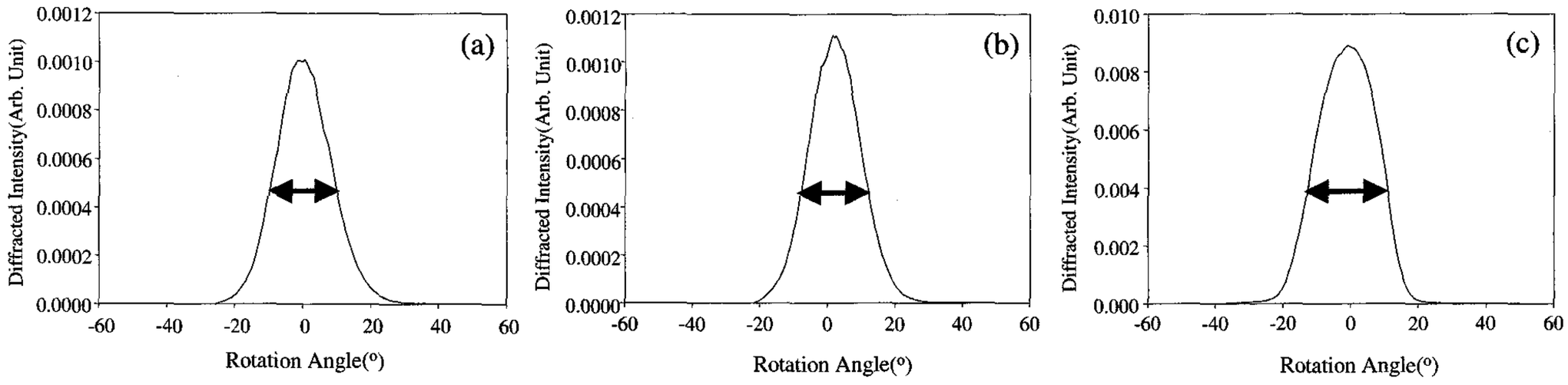

Fig. 7. Diffracted light intensity as a function of the rotation angle of the diffuser. (a) PP-01, (b) PP-02, (c) PP-03.

loosening effect in the polymer binder. Therefore, the large monomers can be diffused and polymerized more effectively in the constructive region. Then, the difference in the refractive index of PP-03 before and after irradiation of the writing beam can increase more compared to those in the two photopolymers having identical concentration of the monomer. Thus, inherently, under identical dose of light irradiation, higher crosslink between the monomers can be expected to induce larger index change.

3.2 Diffuser property fabricated with the photopolymers

We inscribed the surface profile of the glass master diffuser on the surface of the photopolymer. Fig. 3 illustrated the optic setup for elaborating the diffuser gratings and measure the diffracted light intensity with the rotation of the diffuser. First of all, we investigated the photosensitivity of these three photopolymers. Measuring the elapsed irradiation time for saturated diffracted light intensity, we could determine the photosensitivity using the light intensity in terms of mJ/cm^2. The sensitivity data is shown in Table 1. In PP-02, a relatively high sensitivity could be observed. The diffracted light intensity for the sample when rotated from -90° to $+90^\circ$ is plotted in Fig. 7 in each sample. Using this intensity profile, we could determine the diffusing uniformity compared the maximum and minimum intensity. PP-03 showed the best uniformity compared with the other two. The viewing angle we can measure is dependent on the diffusing angle in the master diffuser. When the angle of diffusion is 10° in the master diffuser, we measured the diffusion angle to be in the range of -40° to $+40^\circ$ in our optics geometry. The diffusers with photopolymer, PP-03 showed a relatively good viewing angle of around $\pm 30^\circ$.

Although the performance of the holographic diffuser fabricated in this study is not closely related to the basic properties of the photopolymer, the diffuser with PP-3 showed better performance than the other two. Some properties are thought to be strongly related to the fabrication method and condition. Therefore, the photopolymer showing higher diffraction efficiency is assumed to show higher diffusion property, based on the result of the above experiments. We plan to improve the thermal property of the diffraction efficiency for the practical applications in our future works.

4. Conclusions

The photopolymers were prepared with the monomeric species and the holographic gratings were elaborated in the film samples by the optical interference method. The photopolymer having the synthesized triacrylate monomer showed relatively higher performance in terms of diffraction efficiency. The diffuser fabricated with PP-03 also showed a much greater uniformity and viewing angle compared to those of PP-01 and PP-02. Thus, if the dimensional stability of the PP-03s under light exposure is improved, they would be good candidates for holographic device system in the practical application.

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