Dynamic Behavior of the Diffraction Efficiency in New Photopolymers Elaborated with Photoreactive Binder

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DYNAMIC BEHAVIOR OF THE DIFFRACTION EFFICIENCY IN NEW PHOTOPOLYMERS ELABORATED WITH PHOTOREACTIVE BINDER

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New photopolymers were designed and prepared using a photoreactive poly-
mer binder. The holographic gratings were successfully fabricated in the photo-
polymer sample by conventional optical interference method. The diffraction
property from the gratings in a new photopolymer was investigated by real-
time optical recording to evaluate the effect of photoreaction between the
polymer binder and the newly formed polymer. The dynamic behaviors of
the diffraction efficiency were also studied by using the photopolymers bearing
photoreactive binders with different degree of substitution of the photoreactive
moiety.

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 crosslinker, and sensitizing dye [8]. The host polymer binder acts as a supporting matrix containing the other additive components and the monomers serve as another main species to control the index modulation, induced by optical interference. The refractive index modulation arises from the density and compositional differences of the molecular chains in the adjacent bright and dark regions.

We prepared a new photopolymer using the photoreactive binders in this study. The photoreactive binder consists of poly(vinyl alcohol-co-vinyl acetate) (PVA-co-PVAc) bearing m-isopropylene-α,α-dimethylbenzyl moiety in the side chain. We studied the diffraction properties of the gratings fabricated in photopolymer with a photoreactive binder. The properties were compared with that of the photopolymer composed of poly(vinyl alcohol-co-vinyl acetate) (PVA-co-PVAc) to evaluate the effect of photoreaction between the polymer binder and the newly formed polymer.

EXPERIMENT

Syntheses of Photoreactive Binder

PVA-co-PVAc (10 g, M_w : 90,000) and dibutyltin dilaurate (3.6 g, 0.018 mol) were dissolved in freshly dried tetrahydrofuran (45 ml). To the mother solution, m-isopropylene-α,α-dimethylbenzyl isocyanate (m-TMI, 0.023 g, 0.036 mmol) was added dropwise at room temperature. Reaction was then continued at 70°C for 24–48 hr. The reaction mixture was poured into hexane to make precipitation of the photoreactive polymer. The precipitation was repeated in THF and hexane for purification. The degree of substitution by m-TMI in the hydroxyl group in vinyl alcohol unit was calculated from ^{1}H-NMR spectroscopy. Photoreactive polymers with three different degree of substitution were prepared by control of the reaction time.

Preparation of Photopolymer Film

Three photoreactive polymers were selected to prepare the photopolymer film as shown in Table 1. For preparing the viscous solution to fabricate the thick film, the synthesized photoreactive binders with a different degree of substitution were dissolved in tetrahydrofuran (THF). A proper amount of monomer (BPA-DA), photoinitiator and photosensitizer was added to the binder solution. The exact compositions of the samples used herein were illustrated in Table 1. The resultant viscous solution was filtered through

TABLE 1 Composition of the Photopolymers used in the Study

Sample no	Degree of substitution (%)	Binder (wt%)	Monomer (wt%)	Photoinitiator (wt%)	Sensitizer (wt%)
A	76	64.5	32.3	3.2	0.1
B	52	64.5	32.3	3.2	0.1
C	39	64.5	32.3	3.2	0.1
D	0	64.5	32.3	3.2	0.1

acrodisc syringe filter (Millipore 0.2 μm) and then cast on the borosilicate glass after degassing the solution under vacuum.

Optical Set-Up

The schematic diagram for recording the gratings and measuring the first order diffracted light intensity was illustrated in Figure 1. The Argon laser 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-) 514 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 [9,10]. The probe light was
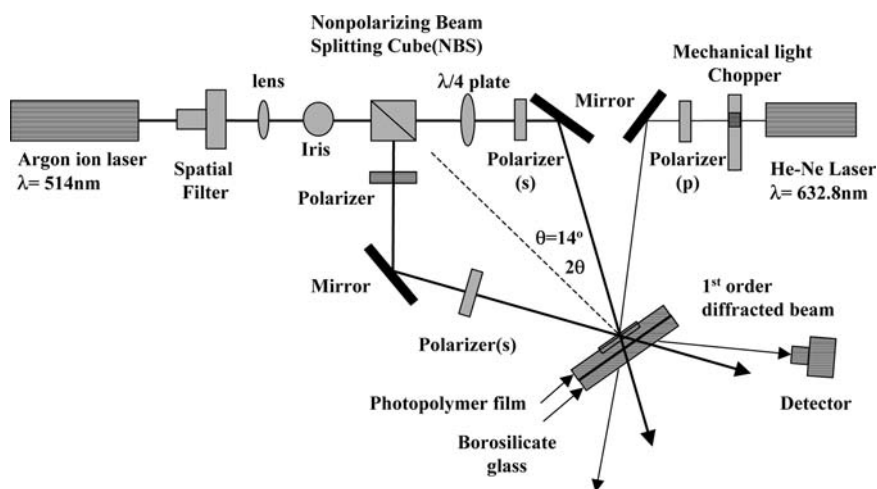

FIGURE 1 Optical setup for measuring the 1st-order diffracted light intensity of the photopolymer.

TABLE 2 Maximum Diffraction Efficiencies and Rising Rates of the Photopolymer Samples

Sample no	Max. Diffraction Efficiency (%)	*Rising rate, k (sec^{-1})
A	44.7	0.271
B	38.1	0.283
C	36.2	0.236
D	34.8	0.142

*The rising time was calculated after fitting the diffraction efficiency to the single exponential rising function. $\eta(t) = \eta_0(1-\exp(-kt))$

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.

RESULTS AND DISCUSSION

Syntheses of Photoreactive Binders

The photoreactive polymer was synthesized by the reaction of PVA-co-PVAc and m-TMI in the presence of dibutyltin dilaurate as a catalyst. The hydroxyl group in vinyl alcohol unit was readily reacted with isocyanate in m-TMI to form a carbamate group. After the reaction with m-TMI, that is, PVA-co-PVAc was grafted in the side chain. (see Fig. 2) Photoreactive polymers with different conversion ratios were prepared by the control of reaction time.

The α-methylstyrene moiety in the side chain of PVA-co-PVAc could be polymerized in the presence of radical initiator.

Typical photopolymer contains photoinitiator and photosensitizer to generate radical species under visible light irradiation. Some specific monomers such as vinyl, acrylate compound existed in the photopolymer can be polymerized radically. If the polymerizable moiety is placed in the
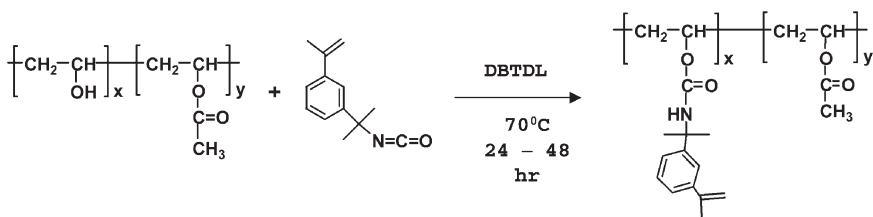
FIGURE 2 Synthesis of the photoreactive polymer binder.

polymer binder, the monomeric or macro radical species can do cross-propagate into the double bond of the photoreactive group in that moiety. Therefore, two polymers will be covalently bound under light irradiation. The diffraction behavior of photopolymer system will be discussed in next section.

DIFFRACTION BEHAVIOR OF THE PHOTOPOLYMER CONSISTED OF THE PHOTOREACTIVE POLYMER BINDER

We studied the diffraction properties of the gratings in photopolymer systems with a photoreactive binder. The properties were compared with those of the photo-inert polymer (PVA-co-PVAc) to evaluate the effect of photoreaction of the polymer binder. The chemical structures of components used in the photopolymer were shown in Figure 3.
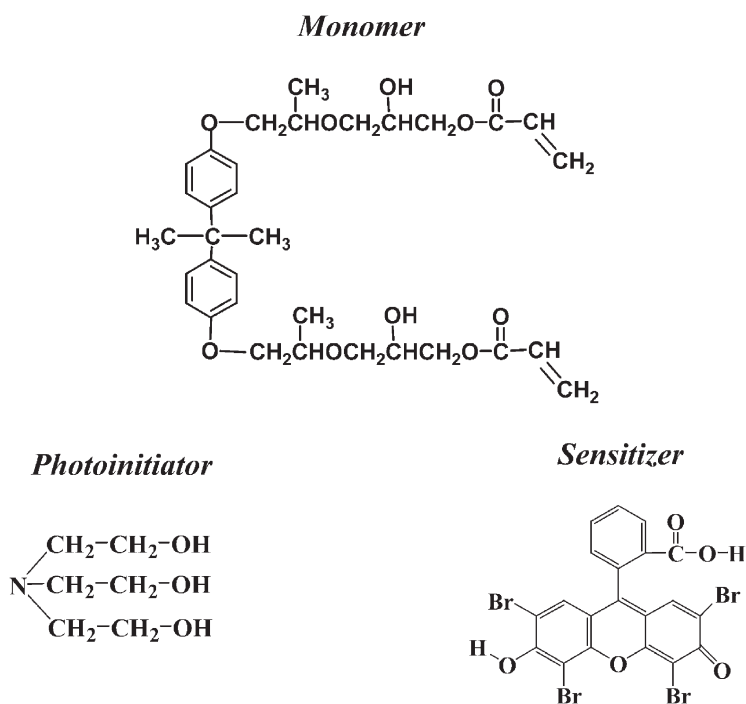

FIGURE 3 Chemical structures of the monomer, photoinitiator, and sensitizer dye used in the study.

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Figure 4 shows the dynamic behaviors of the diffraction efficiency of the photopolymer containing the photoreactive polymer binder with different degree of substitution by m-TMI. First of all, we compared the diffraction behaviors of the sample A and the sample D. The Photopolymer with the polymer binder containing highest substitution of m-TMI (76%) can be conjectured that the glass transition temperature is lower than that of the sample D. Therefore, the diacrylate monomer can be diffused relatively faster to the bright region at an ambient condition. In the bright region, the reaction between the polymer binder and the newly formed polymer occurred to induce the crosslink between two different polymer chains. When the crosslink density increases, the refractive index will increase concomitantly. As a result, we could observe the larger refractive index modulation in the sample A compared to that in the sample D.

As the degree of substitution by m-TMI increased the diffraction efficiency was increased, respectively. It is definitely attributable to the increase of the index modulation that arose from the large increment of the chain density by visible light irradiation. Shortly, photoreactive moieties of α-methylstyrene unit in the polymer binder usually react between
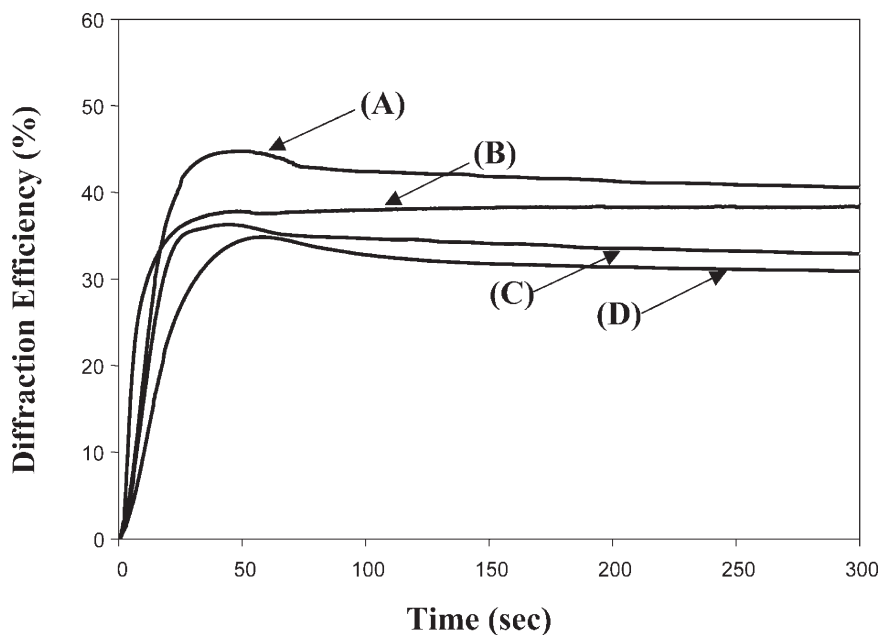

FIGURE 4 Variation of the diffraction efficiency with the change of conversion ratio of the photoreactive polymer binder. (A: 76%; B: 52%; C: 39%; D: 0%)
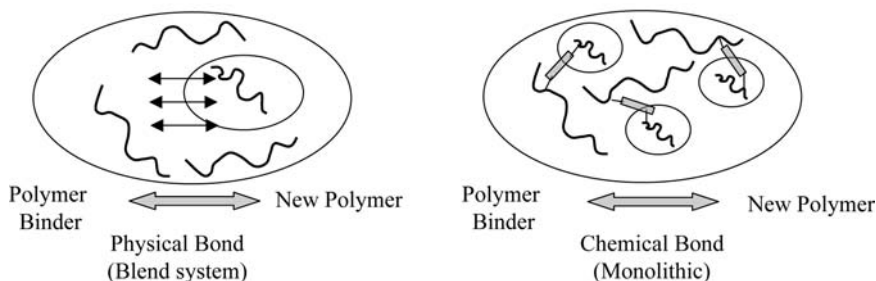
Conventional Photopolymer **New Photopolymer**

FIGURE 5 Comparison between the conventional photopolymer and the photo-polymer system with photoreactive binder.

themselves or/and with newly generated polymer, which enrich the poly-mer chain greatly in the bright region.

CONCLUSION

In conventional photopolymer system, newly generated polymer is blended in the polymer binder physically by virtue of the molecular specific interac-tion. In a new photopolymer used in this study, we could expect the cova-lent bond between the polymer binder and the newly generated polymer through radical species in the bright region. That results in increase of the diffraction efficiency followed by increase of the chain density in the unit matrix.

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