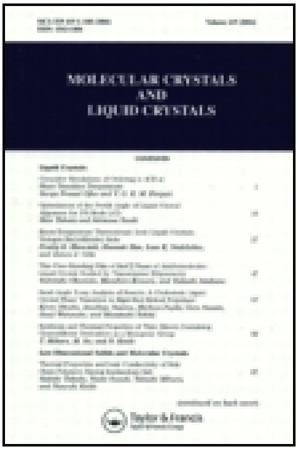

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Fluorescent Photopolymer for Holographic Patterning

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Fluorescent Photopolymer for Holographic Patterning

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Photopolymer films were prepared for holographic recording and fabrication of multi-dimensional holographic fluorescent patterns. The photopolymer consists of a methacrylate epoxy monomer, photoinitiator, sensitizer, binder polymer, and polyanthracene (PAnt) as a fluorophore. The high diffraction efficiency of fluorescent photopolymer film was determined through a holographic recording system as 60% for a film of 85 μm *in thickness. The optimized photopolymer film was applied to fabricate 2 dimensional patterns by laser interference lithography technique and rotation method. A 2-dimensional pattern was confirmed from a fluorescent microscope, which showed crossed pattern having a line width of 0.7 μm.*

Keywords: dual polymerization; fluorescence; holographic lithography; holographic recording; patterning; photopolymer

INTRODUCTION

Holographic grating formation has been interested for new fabrication technique using various media such as polymer dispersed liquid crystal, photochromic media, and photopolymerizable media [1–7]. In particular, photopolymerizable system exploited in holographic storage media has been explored for diffractive elements and memories [8–17]. In the photopolymerizable media, diffractive grating patterns are created as a result of light initiating photopolymerization, through local and non-local polymerization, formed by the interference of laser.

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Since the non-local polymerization followed by diffusion of monomers can be optically triggered and chemically amplified, grating patterns can be made with high homogeneity over large area to afford simple micro pattering process.

We report here a fluorescent photopolymer film and formation of holographic pattern from the photopolymer system containing photopolymerizable monomers and polyanthracene as a fluorophore.

EXPERIMENTAL

Polyanthracene (PAnt) was synthesized from anthracene via Friedel-Crafts reaction as published before [18]. The polyethersulfone (PES, Mw = 35,000) was purchased from Aldrich as a binder polymer. The photopolymer was prepared as a dry film type as follows. A mixture of 2-(oxiranylmethoxy)ethyl 2-methyl–2-propenoate (38.5 wt%), initiator (2.5 wt%), sensitizer (0.08 wt%), PAnt (0.12 wt%) and PES (58.8 wt%, binder polymer) dissolved in a mixture of chloroform and 1,1,2,2-tetrachloroethane. The mixture was stirred in a dark place for 1 hr to yield a yellow homogeneous solution. The homogeneous photopolymer solution was coated on a transparent glass substrate with spacer using polyimide tape (3 M) and the photopolymer film was dried for 8 hr in a dark room. The thickness of the photopolymer film was 85 μm. Phase separation did not occur during the drying process and the film remained transparent before and after recording.

The holographic recording was performed by a series of optical setups consisting of a 491 nm diode laser (50 mw), polarizer, beam splitter and detector, as reported before [19]. Holographic grating was observed after recording through the optical microscope (Bimeince, Model wm0015000a). Holographic patterning was fabricated by rotation method of sample and observed through a fluorescent microscope (Bimeince, Model wm0015000a). Fluorescence spectrum of the film was obtained from a luminescence spectrometer (Perkin–Elmer, Model LS55).

RESULTS AND DISCUSSIONS

Diffraction Efficiency and Fluorescence of Photopolymers

The photopolymer film containing 2-(oxiranylmethoxy)ethyl 2-methyl-2-propenoate monomer in the presence of PAnt as a fluorophore was photochemically sensitive to a visible laser of 491 nm to lead polymerization of the monomer. Under the holographic recording system, the film showed diffraction of a laser beam and the diffraction intensity was rapidly increased within 30 s. Figure 1 shows the evolution of diffraction efficiency for the photopolymer film during the holographic recording under the recording beam of 491 nm. The photopolymer without PAnt showed high diffraction efficiency but after adding Pant, the diffraction efficiency was decreased because the reflective index was changed by the fluorescent polymer (PAnt) and the diffusion of monomers was disturbed by PAnt. Diffraction efficiency of the film containing fluorophore reached a maximum value of 50% for a 85 µm-thick film within 100 s of recording time. The diffraction efficiency was increased over prolonged recording and reached to 60% after 340 s. Thus the photopolymerization in the photopolymer seemed to occur via fast and slow process. Both processes involve monomer polymerization by the non-local and local polymerization. Sensitivity ($S\eta^{1/2}$ (cm^2/J) [20]) and refractive index change of the photopolymer film was determined as 0.003 cm^2/J and 0.0016, respectively, based on the diffraction efficiency of 50% after 100 sec.

$$S = \frac{\Delta n}{tI}\,(\mathrm{cm}^2/J) \tag{1}$$

$$\Delta n = \frac{\lambda \cos\theta \sin^{-1}\sqrt{\eta}}{\pi d} \tag{2}$$

Holographic grating was successfully generated, and the fluorescence intensity was increased by holographic grating patterns as shown in

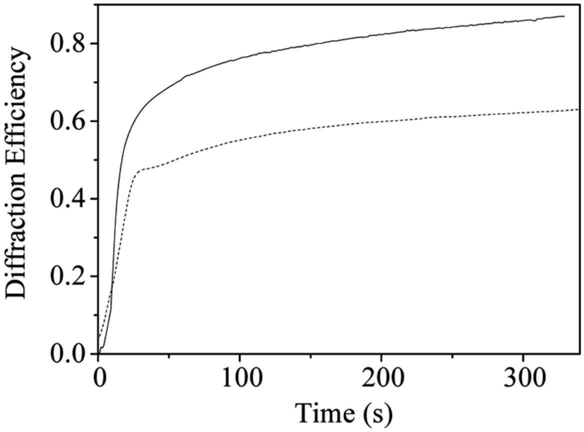

FIGURE 1 Growth of the diffraction efficiency for the fluorescent photopolymer containing PAnt as a fluorophore (dashed line) and without PAnt (solid line) (Thickness of the film = 85 µm) under holographic recording with a light of 491 nm.

Fig. 2. The emission maximum of the spectrum before and after holographic recording was same and observed at 540 nm under the excitation wavelength of 400 nm. Therefore the excited energies of PAnt are not much changed by the photopolymerization of monomers during holographic recording with a light of 491 nm, at which the absorption of PAnt would be negligible. Because PAnt was dimerized only under UV light [18], there was no indication of polyanthracene dimerization under 491 nm in our experiment.

Interestingly, the polymer film, originally less fluorescent, became more fluorescent after holographic recording. The fluorescence intensity of the photopolymer after recording was increased up to 30% than that before holographic recording. Such an increase in fluorescence intensity was obvious when the fluorescence spectra of the film before and after holographic recording were compared as shown in Fig. 2. The increased fluorescence intensity after holographic recording could be ascribed to the formation of micro gratings, which could be originated from the monomer diffusions during the non-local polymerization to lead refractive index modulation between the high and low intensity interference area. During the polymerization of mixtures of a monomer and a fluorophore, the unreactive fluorophore can diffuse to the dark fringes (high intensity interference area), giving rise to periodic planes enriched with fluorophores, as similarly observed for a mixture of a monomer and a liquid-crystalline (LC) compound [21]. If so, fluorescent grating could be observed and they can reduce the interaction between the fluorophores to lead increased fluorescence.

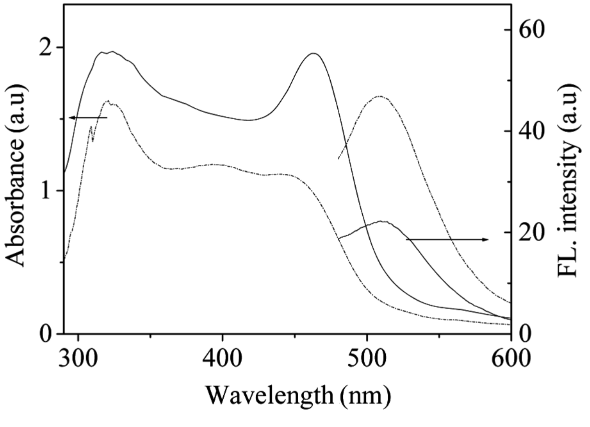

FIGURE 2 UV-Vis and fluorescence spectra of the photopolymer film before (solid line) and after holographic recording (dashed dot line).

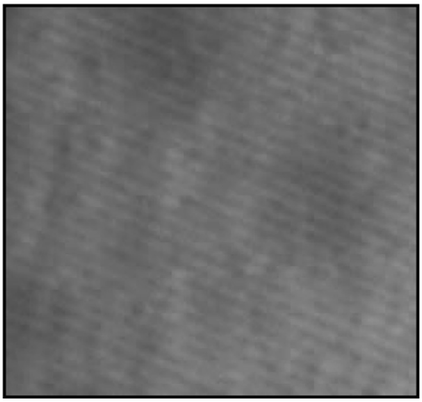

FIGURE 3 The grating pattern on photopolymer containing PAnt after holographic recording.

Indeed grating patterns were observed from microscopic image after holographic recording as shown in Fig. 3. The recorded zone revealed line gratings under microscopy with about 0.72 µm periodic spacing. This experimental value agrees qualitatively with the theoretical value of 0.6 µm from Bragg's law (Eq. (3)) as described below.

$$\mathrm{m}\mathrm{v}_{\mathrm{g}}\lambda = 2\mathrm{n}_{\mathrm{g}}\sin\alpha \qquad (3)$$

where v_{g} is the fringe frequency within the grating volume, n_{g} is the average refractive index of the grating medium, α is the angle of incidence inside the grating with regard to the fringe plane and m the order of diffraction, which equals to 1 in the case of transmission grating [22].

Substituting the refractive index of the photopolymer ($\mathrm{n}_{635} = 1.6052$) determined by a prism coupler using a 635 nm as a probe beam, the angle of incidence ($2\alpha = 30°$), and the wavelength of the recording beam ($\lambda = 491$ nm), the grating period was estimated as 0.60 µm.

2-Dimensional fluorescent grating pattern was fabricated on the photopolymer film through double step holographic recording. The 2nd patterning was performed on the already formed line grating from the 1st grating fabrication process in a 90° angle rotated. When the diffraction efficiency reached the half time of the saturating time of diffraction efficiency, the sample was rotated by 90°. A crossed line patterns with a grating gap of about 0.7 µm could be obtained through double step holographic recording as shown Fig. 4.

The 2-dimensional fluorescent patterns obtained by holographic recording method were stable without erasure of the gratings. This

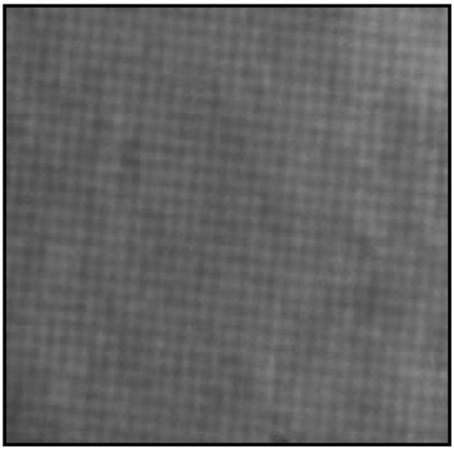

FIGURE 4 The photograph of 2-dimensional pattern through the crossing of grating patterns on a fluorescent photopolymer.

combination of fluorescent materials and reactive monomers is promising as a method to obtain high diffraction efficiency for the holographic storage media and holographic patterning for the organic devices and patterns. Specially, these composite contain the enhanced fluorescent property after holographic recording, therefore fluorescent photopolymer also be applied to security materials using hologram.

CONCLUSION

Fluorescent grating pattern formation on photopolymer films was investigated using a molecular composite of an acrylic monomer and a fluorescent polyanthracene. The fluorescence intensity of the grating area was increased compared to that unexposed area, possibly due to micro separation between the fluorescent polymers by the grating patterns, which may lower the possibility of excited quenching of the polymer by the neighboring polymers. By virtue of the increased emission in the recorded (grating) area, the fluorescent gap electrode pattern was easily detected. From the results, it could be considered that the holographic recording on a fluorophore doped photopolymer can generate regular grating patterns and these grating induce fluorescent intensity increase. Thus the holographic grating formation is a new promising method for pattern formation and fluorescence intensity amplification for emissive organic devices.

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