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Polymeric photorefractive composite for holographic applications

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Abstract

Applications of photorefractive polymeric composite for holographic data storage medium and phase conjugation mirror were demonstrated. Polymeric material composed of photoconducting carbazole-substituted polysiloxane matrix, 2,4,7-trinitro-9-fluorenone, and 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexeny liden}malononitrile chromophore exhibited a diffraction efficiency of 92% at an electric field of 30 V/μm. Holographic recording, reading, and erasing of single page image were demonstrated using the 100 μm thick polymeric composite. We also demonstrated that the distorted phase of the object beam introduced by a image distorter was successfully restored using a phase conjugation mirror. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photorefractive polymer; Holography; Phase conjugation

1. Introduction

Holography has been applied in the field of optical data storage and information processing as large amount of data can be stored via various multiplexing methods, and high data transfer rate is possible due to the parallelism of optics [1,2]. Photorefractive effect refers to a spatial modulation of refractive index in a material due to the light-induced redistribution of charge [3–5]. Since its first discovery in inorganic crystal in 1966, photorefractive effect has been recognized to be promising for various holographic applications due to the large and reversible modulation of refractive index [3,5]. Especially, reversible holographic data storage was suggested to be one of the most important application fields of photorefractive material.

In 1991, Ducharme et al. reported the first polymeric photorefractive material based on the nonlinear optical polymer, bisphenol A diglycidyl diether 4-nitro-1,2-phenylenediamine (bisA-NPDA) doped with a hole transporting diethylamino-benzaldehyde diphenylhydrazone [6]. The diffraction efficiency (η) of the first polymeric photorefractive material was as poor as $5 \times 10^{-5}\%$ and no net gain was observed. However, during the last decade, the performance of photorefractive polymers has rapidly improved. Recently, polymeric materials which showed the high gain coefficient of over 200 cm^{-1} and the response time of several ms have been reported [7–10]. The applications of photorefractive materials in holographic data storage, phase conjugation, pattern recognition, image amplification and so on have been demonstrated. However, the applications of polymeric material are still in its early stages of development [11–14]. One of the drawbacks of polymeric materials, which seriously limit their practical applications, is the necessity of high external field. Most of polymeric photorefractive materials require the high electric fields in the range of 50–100 V/μm, which means that bulk sample of 1 mm thickness will require the impracticably high voltage up to ca. 100 kV. Such a high electric field limits the active layer thickness, and as a consequence, the Bragg selectivity of polymeric material is reduced and the number of holograms multiplexed is decreased, when compared with inorganic crystals [15].

Here, we will present the polymeric photorefractive material, which exhibits the high diffraction efficiency even at low electric field such as 30 V/μm. The applications of polymeric material for holographic recording medium and the phase conjugation mirror were demonstrated.

2. Experimental

2.1. Materials and sample preparation

In this work, low T_g photorefractive material was prepared by doping the optically anisotropic chromophore,2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile (DB-IP-DC), into

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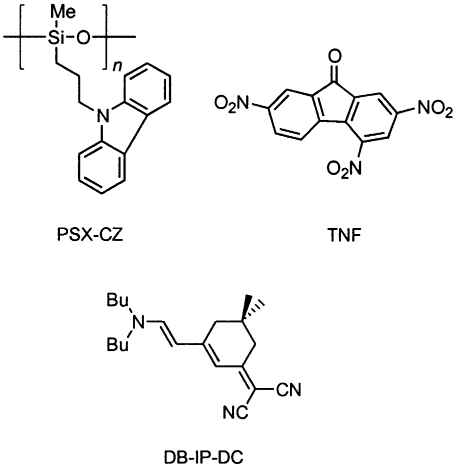


Fig. 1. Chemical structures of components of photorefractive composites: poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-CZ), 2,4,7-trinitro-9-fluorenone (TNF), and 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile (DB-IP-DC) chromophore.

photoconducting polymer matrix, poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-CZ) sensitized by 2,4,7-trinitro-9-fluorenone (TNF). The chemical structures of molecules used in this work are shown in Fig. 1. DB-IP-DC chromophore with large $\mu^2 \Delta\alpha$ (μ is the dipole moment and $\Delta\alpha$ is the polarizability anisotropy) was prepared via condensation reaction of *N*,*N*-dibutylformamide dimethyl acetal and 2-(3,5,5-trimethyl-2-cyclohexyliden) malononitrile synthesized from the reaction of isophorone with malononitrile [16]. TNF purchased from Kanto Chem. Co. Inc. was used after purification. PSX-CZ was synthesized by the previously described method [17]. This polymer was used as a matrix due to its photoconductivity, the relatively low T_g of 51°C, and high optical clarity. T_g of PSX-CZ composite can be lowered to room temperature simply by adding the chromophore. No extra plasticizer was needed, different from high-T_g polymers such as polyvinylcarbazole (PVK). Note that in the case of low T_g composite, the glass transition temperature should be in the vicinity of measuring temperature in order to take advantage of orientational enhancement effect [7].

In order to prepare the sample, the mixture consisting of PSX-CZ: DB-IP-DC: TNF in a ratio of 69:30:1 wt% was dissolved in dichloromethane, and the solution was filtered through a 0.2 μm filter. The composite was casted on indium tin oxide (ITO) glass plate, dried for 6 h at ambient temperature and subsequently heated in an oven at 90°C for 24 h to remove the residual solvent completely. Then, composite was softened by placing it on a hot plate at 100°C and then covered with the second ITO coated glass. The thickness of the film was controlled by Teflon spacer between two ITO glass plates. The glass transition temperature (T_g) of composites was determined by differential scanning calorimetry (Perkin Elmer DSC7) at the heating rate of 10°C/min. The polymer composite containing 30 wt% of DB-IP-DC chromophore showed the glass transition temperature of 27°C without any extra plasticizer.

2.2. Measurements

In this work, all experiments, i.e. degenerate four-wave mixing (DFWM) and holographic experiments were performed using 100 μm-thick composite.

The diffraction efficiency of photorefractive material was determined by the DFWM experiment. Two coherent laser beams at the wavelength of 632.8 nm were irradiated on the sample in the tilted geometry with the incident angle of 30 and 60° with respect to sample normal. Both the writing beams were *s*-polarized and had the equal intensity of 60 mW/cm^2. The recorded photorefractive grating was read out by a *p*-polarized counter-propagating probe beam. Attenuated reading beam with the very weak intensity of 0.1 mW/cm^2 was used. The internal diffraction efficiency (η_{int}) of photorefractive material was determined from Eq. (1) [18]:

$$\eta_{\mathrm{int}} = \frac{I_{\mathrm{R,diffracted}}}{I_{\mathrm{R,diffracted}} + I_{\mathrm{R,transmitted}}} \tag{1}$$

where $I_{\mathrm{R,diffracted}}$ and $I_{\mathrm{R,transmitted}}$ are the diffracted and transmitted intensities of reading beam, respectively.

Holographic applications of polymeric material were performed at the wavelength of 632.8 nm using experimental setup shown in Fig. 2. The *s*-polarized laser light was split into object and reference beams with the equal intensity of 4 mW/cm^2. The spatially filtered object beam was expanded into 30 mm in beam diameter and then was passed through the mask with a dimension of 15 mm × 15 mm. The hologram was recorded by the intersection of object beam containing the information and reference beam in the photorefractive sample. The incident angles of the object and reference beams were 45 and 135° with respect to sample normal, respectively. The internal angle of 90° was used in

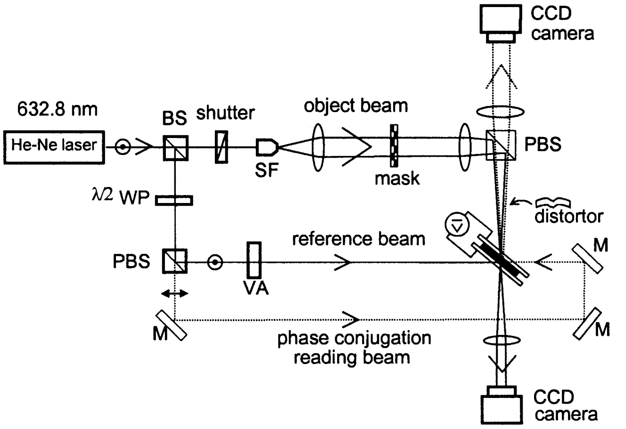


Fig. 2. Schematic diagram of optical setup used for holographic applications. BS: nonpolarizing beam splitter; PBS: polarizing beam splitter; SF: spatial filter; VA: variable attenuator; λ/2 WP: half-wave plate; M: mirror, CCD: charge-coupled-device camera.

order to maximize the angular selectivity [19]. The recorded hologram image was read back by illuminating of *s*-polarized attenuated light with the intensity of 0.01 mW/cm^2 and the reconstructed hologram image was recorded on a charge-coupled device (CCD) camera.

For phase conjugation experiment, a deformed glass plate was inserted as a distorting medium in front of the sample. The *p*-polarized reading beam counter-propagating with respect to the reference beam was used. The intensity of reading beam was 0.01 mW/cm^2.

3. Results and discussion

Diffraction efficiency is one of the most important factors determining the performance of holographic materials, and here, it was measured by DFWM. As presented in Fig. 3, the 100 μm-thick photorefractive composite containing 30 wt% of DB-IP-DC chromophore shows the diffraction efficiency of 92% at 30 V/μm. The outstanding photorefractive property of DB-IP-DC composite is attributable to the large electro-optic effect, as described in our previous study [16]. In the case of low T_g photorefractive material, the modulation of refractive index (Δn) is known to arise predominantly from the reorientation of the optically nonlinear chromophore under the spatially modulated space-charge field [7–10]. The large orientational birefringence of current polymeric composite, which is associated with the large $\mu^2\,\Delta\alpha$ of DB-IP-DC chromophore where $\Delta\alpha$ is the polarizability anisotropy and μ is the dipole moment, may lead to the high diffraction efficiency at a moderate electric field of 30 V/μm.

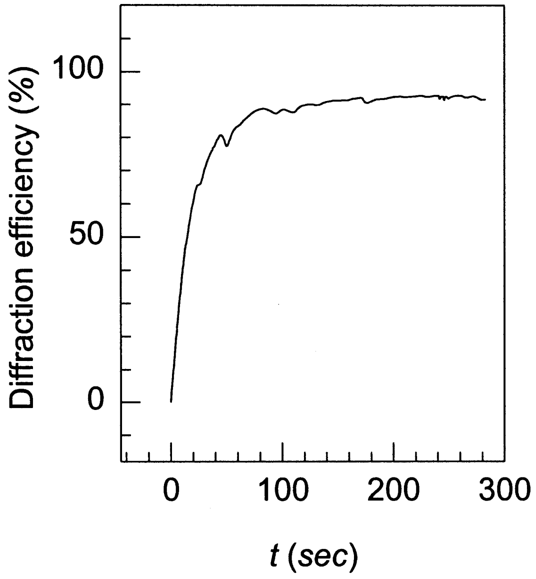
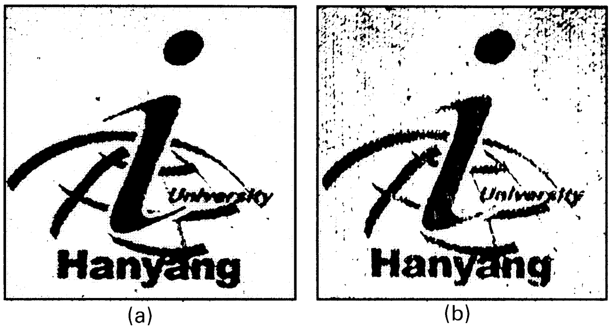


Fig. 3. Diffraction efficiency of polymeric composite at 30 V/μm.



(a) (b)

Fig. 4. Photographs of (a) original image transmitted through the sample and (b) reconstructed hologram image.

The large dynamic range ($\Delta n \sim 3 \times 10^{-3}$) of our photorefractive material at 30 V/μm is a quite encouraging result. As is well known, most of polymeric photorefractive materials require the high electric fields in the range of 50–100 V/μm, which is considered as one of the major drawbacks of polymeric system [7–9,15]. The lowering of required electric field enables the fabrication of the thicker photorefractive film, which will consequently enhance the overall hologram quality, i.e. the better Bragg sensitivity and the higher number of multiplexed holograms.

The potential of our composite as a holographic recording medium was assessed with the hologram recording and phase conjugation experiments. First, hologram image was recorded at the external field of 30 V/μm using 100 μm thick composite. Fig. 4(a) and (b) are the image after transmission through the mask and the sample and the reconstructed hologram image, respectively. This result shows that the reconstructed image has the contrast as high as that of the original image, indicating the performance of the current polymeric material in holographic application. The recorded hologram can be completely erased by illumination of reference beam alone. However, the response of

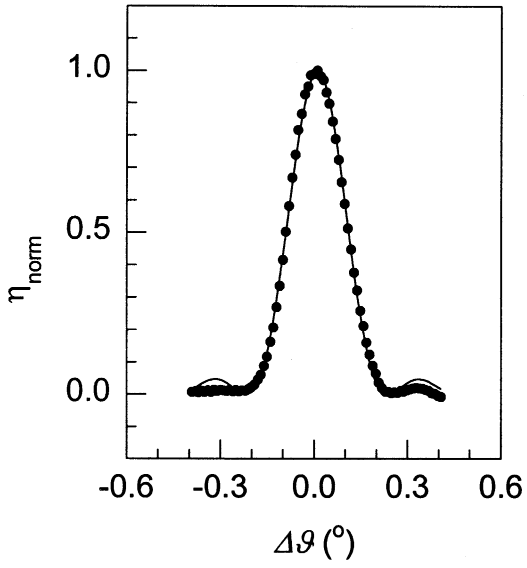
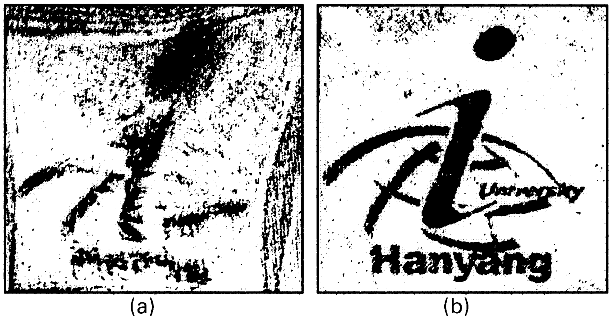


Fig. 5. Variation of diffraction efficiency as a function of angular deviation ($\Delta\vartheta$) of incident angle from Bragg angle. η_{norm} is the diffraction efficiency normalized using η at Bragg angle. Filled circles are measured data and line is for fitted curve obtained using Eq. (2).



(a) (b)

Fig. 6. Photographs of (a) distorted image by a deformed glass, and (b) restored phase-conjugation image.

holographic grating formation of our composite is rather slow: it takes about several seconds to write a hologram, which needs to be improved.

High storage densities in holographic materials can be achieved by various multiplexing methods [1,2]. The angular selectivity is an important parameter to determine the efficiency of angular multiplexing method. In this work, the angular selectivity of the photorefractive material was determined by measuring the variation of diffraction efficiency as a function of angular deviation ($\Delta\vartheta$), where $\Delta\vartheta = \vartheta - \vartheta_0$ denotes the deviation of the internal angle (ϑ) of incident reading beam from the exact Bragg angle (ϑ_0). As presented in Fig. 5, diffracted beam shows the maximum intensity when the incident angle of reading beam satisfies the Bragg angle (ϑ_0). As the incident angle is deviated from a Bragg condition, diffracted intensity is dramatically decreased, depending on the angular deviation ($\Delta\vartheta$). The angular selectivity is determined by the value of angular deviation ($\Delta\theta_{\mathrm{ref}}$) where the diffracted beam intensity is decreased first to zero. At current experimental conditions, $\Delta\theta_{\mathrm{ref}}$ is observed to be 0.227°, as shown in Fig. 5. This is in good agreement with the calculated value of $\Delta\theta_{\mathrm{ref}} = 0.219°$, obtained using Eq. (2) [19]:

$$\Delta\theta_{\mathrm{ref}} = \frac{4\lambda}{n\pi L}\,\frac{\cos\theta_{\mathrm{ref}}}{|\sin(\theta_{\mathrm{obj}} + \theta_{\mathrm{ref}})|} \tag{2}$$

where L is the thickness of sample, and θ_{obj} and θ_{ref} are the incident angles of the object and the reference beams with respect to sample normal, respectively.

The application of polymeric composite for a phase conjugation mirror was successfully performed, as shown in Fig. 6. The phase of object beam was distorted by passing through a distorting medium and consequently, its hologram image recorded in the photorefractive material was also distorted, as shown in Fig. 6(a). However, the phase distortion of the object beam was compensated, as the time-reversed replica of the transmitted object beam, generated by the reading beam counter-propagating with respect to the reference beam, propagates through distorting medium. Fig. 6(b) shows the restored hologram image using phase conjugation mirror.

4. Conclusion

Polymeric photorefractive materials are expected to play an important role in photonic technology, due to their high photosensitivity, large dynamic range (Δn), and low manufacturing cost. In this work, we have demonstrated the applications of polymeric composite based on photoconducting polysiloxane doped with 30 wt% of DB-IP-DC for holographic storage and phase conjugation. The high diffraction efficiency of the current composite even at the low applied field will appear to provide the substantial advantage for holographic information processing.

Acknowledgements

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