Applications of Polymeric Photorefractive Material to Reversible Data Storage and Information Processing

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ABSTRACT: A polymeric photorefractive composite was prepared from a mixture of carbazole-substituted polysiloxane as a photoconducting medium, 2,4,7-trinitro-9-fluorenone as a photosensitizer, and 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile as an optically nonlinear chromophore. This polymeric composite, with a thickness of 100 μm, exhibited a high diffraction efficiency of 92% at a low applied electric field of 30 V/μm, which corresponded a refractive index modulation of 3×10^{-3}. Applications of this polymeric composite to reversible holographic data storage and pattern recognition were demonstrated. The three-dimensional image was recorded on our photorefractive film at an applied field of 30 V/μm, and subsequently, a high quality image was reconstructed in a real-time operation. Pattern recognition was successfully demonstrated based on a joint-transform optical correlation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 368–372, 2003

Key words: photorefractive effect; polysiloxanes; inorganic polymers

INTRODUCTION

The photorefractive effect refers to the spatial modulation of the refractive index (Δn) of materials that possess both photoconductivity and optical nonlinearity simultaneously.[1,2] Under the nonhomogeneous illumination formed by the interference of two coherent laser beams, a spatially modulating space–charge field is formed because of the redistribution of photocharges, which subsequently modulate the refractive index of material via an electrooptic effect. The attractive features of the photorefractive effect are that (1) a large Δn (up to the order of 10^{-2}) can be induced by a low-power laser on the order of milliwatts and (2) the photorefractive grating formed can be completely erased by the illumination of single laser beam. Consequently, photorefractive material has been considered a promising recording medium, especially for reversible optical storage and information processing in real-time applications.[1,3,4]

Holographic data storage is one promising application for photorefractive materials.[3–7] Holography involves the recording of the interference pattern between a signal beam carrying the information and a reference beam and retrieval of the stored information by illumination of a reference beam. It has been extensively applied to optical data storage because a large amount of data can be stored via various multiplexing methods and optical information can be retrieved with a high data-transfer rate due to the parallelism of optics.[5]

Pattern recognition is another area where the parallelism of optics, that is, optical processing, provides a significant advantages over digital electronics.[7,8] It has been developed for security systems applications such as the identification of human pupils and fingerprints, rapid searching of huge database, navigation, image analysis, and so on. Because of its high photosensitivity, low cost, and high processability, photorefractive polymers have been considered as promising candidates for pattern-recognition systems.[4,7,8]

Until recently, the application of photorefractive materials to holographic data storage, phase conjugation, pattern recognition, image amplification, and so on have been demonstrated, and most studies have been confined to photorefractive inorganic crystals.[3] However, the widespread application of inorganic crystals has been limited by their high cost and poor processability, despite proof-of-principle demonstrations. In contrast, holographic applications of polymeric photorefractive materials, which can overcome the disadvantages associated with inorganic materials, have still been limited. The development of new polymeric materials and their applications are strongly needed for commercialization.

In this work, we present a highly efficient polymeric photorefractive composite with a low glass-transition temperature (T_g). The holographic application of this polymer composite to reversible holographic data storage and pattern recognition were demonstrated at a low applied electric field.

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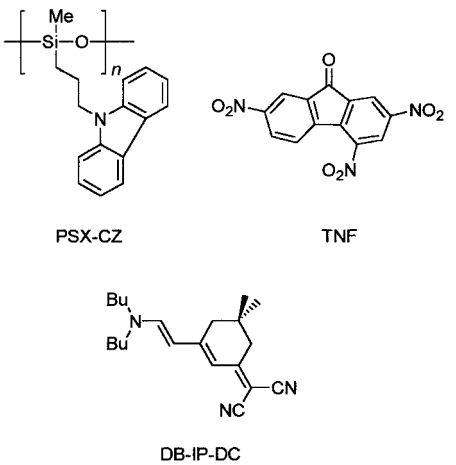


Figure 1 Chemical structures of the components for photorefractive composites: PSX-Cz charge-transporting matrix, DB-IP-DC chromophore, and TNF.

EXPERIMENTAL

Materials

The molecular structures of the components used in this study are shown in Figure 1. 2-{3-[(*E*)-2-(Dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile (DB-IP-DC) chromophore was prepared via a 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.[9] This chromophore was designed to possess a large $\mu^2\Delta\alpha$ (where μ is the dipole moment and $\Delta\alpha$ is the polarizability anisotropy) to maximize the orientational enhancement effect. 2,4,7-Trinitro-9-fluorenone (TNF), which was used as a photosensitizer (Kanto Chem Co., Inc., Tokyo, Japan), was purified before use. Poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-Cz), a photoconducting matrix, was synthesized by the previously described method.[10] This polymer was chosen as a matrix because of its photoconductivity, the relatively low *Tg* of 51°C, and high optical clarity.[11] The *Tg* of PSX-Cz composite could be lowered to room temperature simply by the addition of the chromophore. No extra plasticizer was needed, which differs from high-*Tg* polymers such as polyvinylcarbazole.[4,8,12,13] In the case of low-*Tg* photorefractive composites, the lowering of *Tg* to the vicinity of the measuring temperature is required to take advantage of orientational enhancement effect.[12–14]

Sample preparation

The polymer composite used in this study was based on photoconducting carbazole-substituted polysiloxane (PSX-Cz) doped with DB-IP-DC chromophore and TNF. The composition of the sample was PSX-Cz:DB-IP-DC:TNF at a ratio of 69:30:1 wt %. The mixture was dissolved in dichloromethane, and the solution was filtered through a 0.2-μm filter. This solution was cast on an indium tin oxide (ITO) glass plate and dried for 6 h at ambient temperature. Subsequently, the obtained film was heated in an oven at 90°C for 24 h to remove the residual solvent completely. Then, we softened it by placing it on a hot plate at 100°C and then sandwiched it between ITO-coated glass under light pressure to yield a film with uniform thickness. The thickness of the film was controlled by a Teflon spacer between the two ITO glass plates.

The *Tg* of the material was determined by differential scanning calorimetry (PerkinElmer DSC7, Norwalk, CT) at a heating rate of 10°C/min. The polymer composite containing 30 wt % DB-IP-DC chromophore showed a *Tg* of 27°C without any extra plasticizer.

Measurements

In this work, all experiments were performed at an applied field of 30 V/μm, with 100 μm thick film. The light source was a He–Ne laser (λ = 632.8 nm).

The diffraction efficiency of the photorefractive material was determined by a degenerate four-wave mixing (DFWM) experiment.[7] Two coherent laser beams were irradiated on the sample in a tilted geometry with incident angles of 30 and 60° with respect to the normal sample. The writing beams both were *s*-polarized and had equal intensities of 60 mW/cm^2. The photorefractive grating recorded was read out by a *p*-polarized counterpropagating probe beam. An attenuated reading beam with a very weak intensity of 0.1 mW/cm^2 was used. The internal diffraction efficiency (η_{int}) of the photorefractive material was determined from eq. (1):[12]

$$\eta_{\text{int}} = \frac{I_{P,diffracted}}{I_{P,diffracted} + I_{P,transmitted}} \quad (1)$$

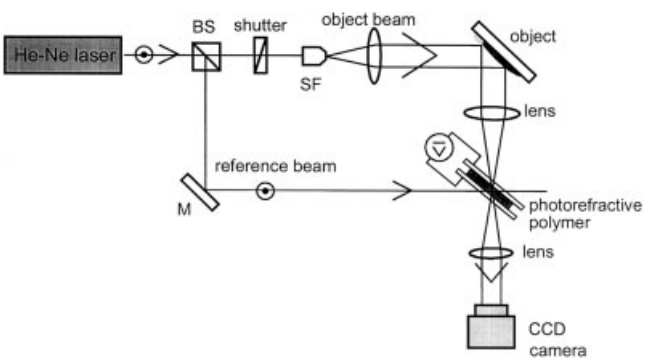


Figure 2 Schematic diagram of the holographic storage setup: BS = beam splitter; SF = spatial filter; M = mirror.

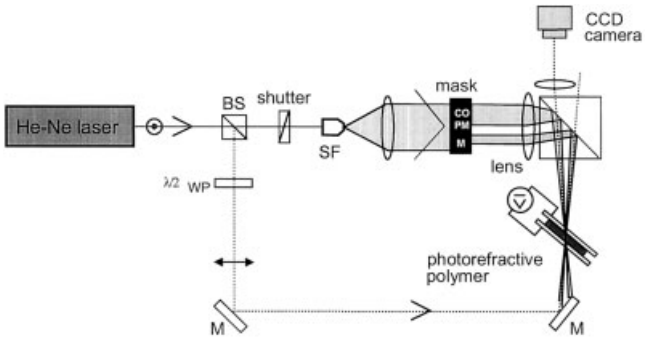


Figure 3 Schematic diagram of the optical correlation setup: BS = beam splitter; SF = spatial filter; M = mirror.

where $I_{P,\text{diffracted}}$ and $I_{P,\text{transmitted}}$ are the diffracted and transmitted intensities of the probe beam, respectively.

Reversible holographic optical data storage was performed with the experimental setup shown in Figure 2. The *s*-polarized laser light was split into object and reference beams. The spatially filtered object beam was expanded into a beam 30 mm in diameter and was then reflected from the surface of the Korean coin with a diameter of 18 mm. The hologram was recorded by the intersecting of the object beam containing the information and a reference beam in the photorefractive sample. The incident angles of the object and reference beams were 45 and 135°, respectively, with respect to the normal sample. An internal angle of 90° was used to maximize angular selectivity.[15] The hologram image recorded in the photorefractive polymer was read back by the attenuated reference beam with an intensity of 0.05 mW/cm^2, and the reconstructed hologram image was recorded on a charge-coupled device (CCD) camera.

The pattern recognition system we used in this study was based on a joint-transform optical correlation.[7,16] The optical configuration is shown schematically in Figure 3. The *s*-polarized writing beam, which was spatially filtered and expanded into a beam 40 mm in diameter, was passed through the mask with a

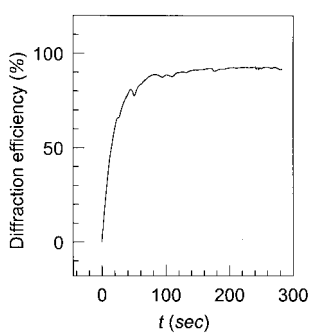
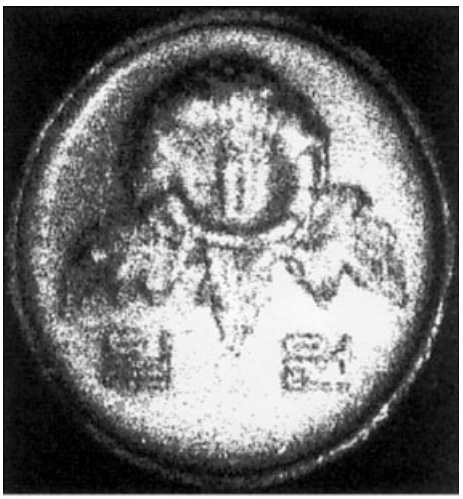
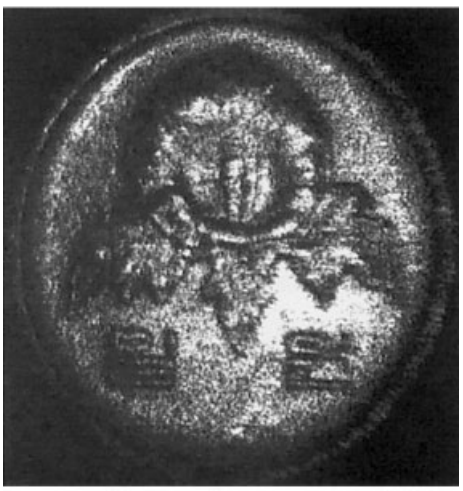


Figure 4 Diffraction efficiency of the polymeric composite at an applied electric field of 30 V/μm.



(a)



(b)

Figure 5 (a) Original image of a three-dimensional object, a Korean coin, to be recorded. (b) Holographic image reconstructed from the hologram recorded in the photorefractive sample.

dimension of 15 × 15 mm. The intensity of the writing beam was 15 mW/cm^2. The object and master patterns to be correlated were placed at the input plane at the same time. The photorefractive sample placed in the Fourier plane was tilted such that the bisector of writing beams formed an angle of 20° with respect to normal sample. The writing beam, passed through a transmission mask, was focused on the photorefractive film. The correlation product of the object and the master patterns was read out by a *p*-polarized reading beam, counterpropagating with respect to the object beam. The diffracted beam projected onto a CCD camera showed the correlated result. The intensity of the reading beam was 0.1 mW/cm^2.

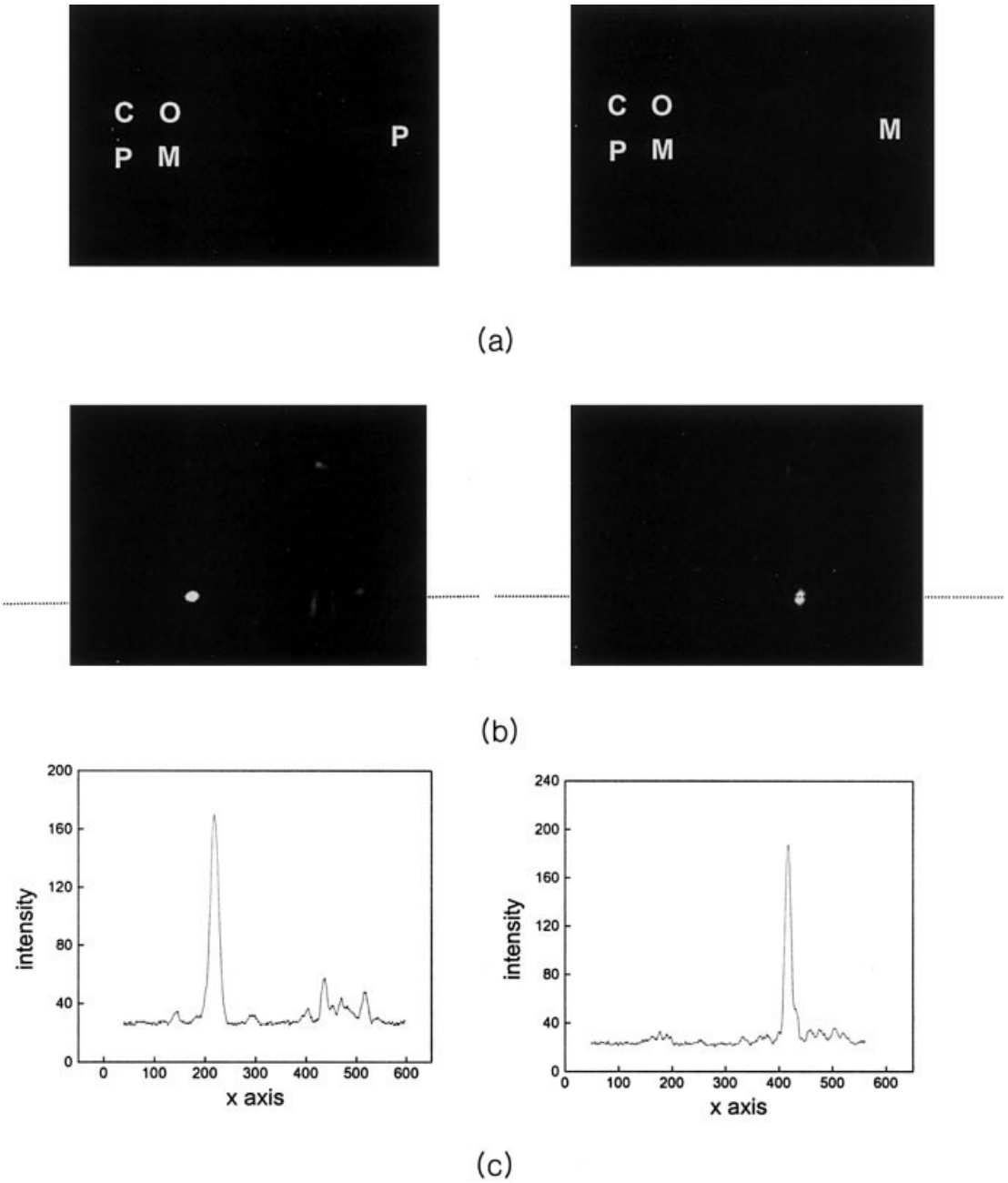


Figure 6 (a) Master (COPM) and object patterns (P or M) to be correlated. (b) Optical correlation results of the master and the object patterns detected by the CCD camera. Bright spots were observed at the location where the targets (P or M) matched the master pattern. (c) Intensity distribution along the dotted line in (b).

RESULTS AND DISCUSSION

Photorefractive properties of the polymer composite

The performance of the photorefractive material was evaluated by diffraction efficiency, as measured by the DFWM method. As presented in Figure 4, the 100 μm thick photorefractive material containing 30 wt % DB-IP-DC chromophore showed a diffraction efficiency of 92% at 30 V/μm, which corresponded to a Δn of 3 $\times$ 10^{-3}. The large dynamic range of our photorefractive material was quite an encouraging result because most polymeric photorefractive materials require a higher electric fields in the range of 50–100 V/μm, which has been considered a serious drawback of polymeric systems.[4,8,12,13] The high diffraction efficiency may have arisen from the high electrooptical activity of the DB-IP-DC chromophore, as described in our previous article.[9] That is, our polymer composite showed a large orientational birefringence associated with a large $\mu^2\Delta\alpha$ value of polyene-based DB-IP-DC chromophore. In the case of the low-*Tg* photorefractive polymer, steady-state photorefractive properties,

such as diffraction efficiency, are governed predominantly by the reorientation of the optically nonlinear chromophore under a spatially modulated space–charge field, which is called an orientational enhancement mechanism.[12–14]

Applications to reversible data storage and pattern recognition

We evaluated the potential of our material as an erasable holographic medium by recording, reading, and erasing the optical image in a real-time operation. Figure 5(a) shows the three-dimensional object, a Korean coin, to be recorded. The storage of image was carried out in an external field of 30 V/μm with a 100 μm thick composite. The stored information was read back with the weak reading beam, as shown in Figure 5(b). The reconstructed image showed a good contrast, comparable to the original image, indicating the performance of this polymeric material as holographic recording medium. The recorded hologram could be completely erased by the illumination of a single beam. However, the response of the holographic grating formation of our composite was still rather slow, which needs to be improved.

Pattern recognition was carried out by the joint Fourier transform optical correlation, proposed by Weaver and Goodman.[16] The optical correlation was carried out with a 100 μm thick sample in a real-time operation at 30 V/μm. Figure 6(a) shows the master (COPM) and object patterns (P or M) to be correlated. By passing the recording beam through the mask, we Fourier transformed the master and object images to be correlated, and subsequently, the interference pattern of their Fourier transforms were recorded in the photorefractive sample. The subsequent readout of this hologram with a weak probe beam yielded the results of the optical correlation of the object and the master patterns. As shown in Figure 6(b,c), a strong correlation was observed only at the location where the target (P or M) matched the master pattern. This result indicates that the optical correlation of the target image with master, that is, a database, was demonstrated successfully with our photorefractive polymer as a recording material.

CONCLUSIONS

In this work, we presented the possibility of our photorefractive polymer as a novel optical material. High-contrast reversible holographic data storage and optical information correlation were successfully demonstrated, with the polymeric composite based on PSX-Cz doped with 30 wt % DB-IP-DC. The high diffraction efficiency of this composite even at a low applied field appeared to provide a substantial advantage for information processing.

Polymeric photorefractive materials have been recognized as attractive candidates for holographic storage and signal processing because of their high photosensitivity, large dynamic range (Δn), and reversibility. In addition, the low manufacturing cost, structural flexibility, and excellent processability associated with polymeric materials will provide further advantages for commercialization, which requires mass production and various sizes from a large-area film to a very small size for miniaturizing the system. Therefore, we think the excellent photorefractive properties of our photorefractive polymer and its successful demonstrations may put us one step further toward the application of polymeric materials to various optical applications.

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