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Asymmetric Energy Transfer in Photorefractive Polymer Composites Under Non-Electric Field

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We prepared photorefractive composites using poly(methyl methacrylate) (PMMA) as a host material doped with 3-[(4-Nitrophenyl)azo]-9H-carbazole-9-ethanol (NACzE) as an NLO chromophore. Photorefractive properties were characterized by means of a two beam coupling (2BC) and a degenerated four wave mixing (DFWM) methods performed at 632.8 nm and room temperature. We successfully observed asymmetric 2BC under non-electric field: photorefractive characteristics obtained are a net 2BC gain of 426 cm^{-1}and a diffraction efficiency of 35%. We could also demonstrate its high performance by DFWM image processing experiment. In order to reduce the glass transition temperature T_g of photorefractive composites we selected poly(ethyl methacrylate) (PEMA) as a host material. Photorefractive properties obtained are a net 2BC gain of 398 cm^{-1} and a diffraction efficiency of 40%.

Keywords: DFWM; image processing; NACzE; net 2BC gain; non-electric field

INTRODUCTION

Photorefractive effect in polymer-based composites was firstly reported by Ducharme *et al.* in 1991 [1], since then it has been investigated intensively because of their wide variety of potential applications such as dynamic hologram, high density optical data storage, optical amplification, phase conjugated mirrors, and image processing. Asymmetric energy transfer between two incident beams passing through the photorefractive medium is a unique characteristic of the photorefractive effect, which is caused by the asymmetric diffraction due to refractive index gratings formed in the medium following the

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interference of two incident light beams through photoconductive and electro-optic effects [2–4]. The polymer-based photorefractive composites have advantages such as structural flexibility, low dielectric constants, ease of synthesis, processability, and low cost, and hence they have attracted many investigators in both academia and industries. The practical applications, however, are still far from the reality. One of the reasons is considered that in general the photorefractive effect occurs under relatively high applied electric field of $10^5 \sim 10^6$ V/cm in the photorefractive device configuration. Recently, some research groups reported the photorefractive effect in organic materials without any electric fields [5–7].

In this study, we try to find material systems which show photorefractive (PR) effect without electric field. From the viewpoint of monolithic system for longer life time of PR materials, we selected 3-[(4-Nitrophenyl)azo]-9H-carbazole-9-ethanol (NACzE) as a nonlinear optical chromophore. It should be noted that the monolithic PR molecules have both photoconductive properties (i.e., carrier generation by photoexcitation and carrier transport) and second order nonlinear optical properties (i.e., Pockels effect), which leads to no phase separation often observed in the multicomponent PR systems [8]. If NACzE has a high PR performance, then we can select various kinds of polymers as the transparent and high optical quality matrix. Then our first choice was poly(methyl methacrylate) (PMMA) as a matrix of NACzE. Photorefractive properties of NACzE/PMMA films were characterized by a two beam coupling (2BC) experiment and a degenerated four wave mixing (DFWM) experiment at wavelength of 632.8 nm. In addition, we demonstrated the image reconstruction of distorted images using phase conjugation technique.

In order to investigate the PR mechanism without applying electric field, we introduced the lower T_g (glass transition temperature) polymers as a matrix.

EXPERIMENTAL

Sample Preparation: Since a rather thick film is required for the photorefractive measurement, we used PMMA and poly(ethyl methacrylate) (PEMA) as a host material and NACzE as a PR chromophore in the sample preparation. Here all the materials were purchased from Aldrich and no further purification was performed. Materials used in this study are shown in Figure 1. The ratio of NACzE and PMMA (or PEMA) was systematically changed to find an optimum condition. The 11 samples used are summarized in Table 1, where the ratio is in wt%. These materials were dissolved

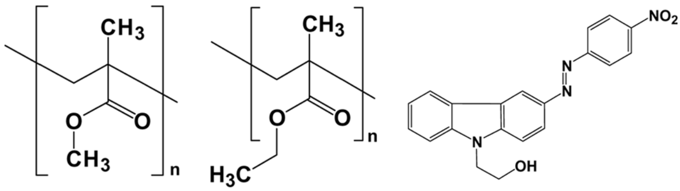

FIGURE 1 Structural formulae of materials used in this study.

in *N,N*-dimethylformamide (DMF), and the mixed solution was casted onto a glass substrate at 100°C, then dried in nitrogen atmosphere at 100°C for 2 h, dried *in vacuo* for overnight at 120°C. The film was sandwiched with another glass, followed by the hot press at 200°C in nitrogen atmosphere for about 10 min. Here, the film thickness was controlled by using a 50 μm-thick polyimide spacer.

Photorefractive Measurement: Photorefractive properties of these samples were characterized by means of 2BC and DFWM methods. The UV-Vis optical absorption spectra indicated that each sample had reasonable absorption in 633 nm, then the laser wavelength was selected at 632.8 nm (He-Ne) for both measurements. In the 2BC experiment, the incident laser beam is split into two beams and the polarization is controlled by polarizer to *p*-polarization (PMMA system: 51.0 mW/cm^2, PEMA system: 25.5 mW/cm^2). The two beams are crossed at the sample set on the piezo-stage for rotation and translation. The crossing angle of two beams is 11.3°, and the sample is tilted by 0° with respect to the bisector of the two writing beams.

TABLE 1 Samples used and Their Photorefractive Characteristics

Composition	Absorption coefficient (α)	Phase shift (deg)	2BC gain (cm^{-1})	Net 2BC gain (cm^{-1})
PMMA/NACzE (90:10)	16	15	62	46
PMMA/NACzE (80:20)	21	29	124	103
PMMA/NACzE (75:25)	23	68	215	192
PMMA/NACzE (70:30)	25	72	451	426
PMMA/NACzE (65:35)	27	65	225	198
PMMA/NACzE (60:40)	31	59	213	182
PEMA/NACzE (90:10)	15	56	132	117
PEMA/NACzE (85:15)	18	63	214	196
PEMA/NACzE (80:20)	21	80	419	398
PEMA/NACzE (75:25)	25	70	378	353
PEMA/NACzE (70:30)	27	69	293	266

From the 2BC measurement, we can calculate the 2BC gain (Γ) as follows:

$$\Gamma = \frac{\cos\theta_2}{d}\ln\left(\frac{I_{2,with}}{I_{2,without}}\right) - \frac{\cos\theta_1}{d}\ln\left(\frac{I_{1,with}}{I_{1,without}}\right) \tag{1}$$

where I_i ($i = 1,2$) are the intensity of each beam i with or without the second beam, θ_i the refraction angle of each beam and d the film thickness.

In the DFWM measurement the sample was irradiated by two s-polarized beams (PMMA system: 51.0 mW/cm^2, PEMA system: 25.5 mW/cm^2) of wavelength 632.8 nm to form the grating, and irradiated by one p-polarized beam (2.5 mW/cm^2). Then the diffracted beam was detected by a photodiode. The diffraction efficiency (η) is calculated as follows:

$$\eta = \frac{I_{diffract}}{I_{incident}} \tag{2}$$

where $I_{incident}$ and $I_{diffract}$ are the intensity of incident and diffracted beams, respectively. The phase shift of refractive index grating was determined from the 2BC measurement. Image processing experiment was carried out under the same environment (wavelength of laser

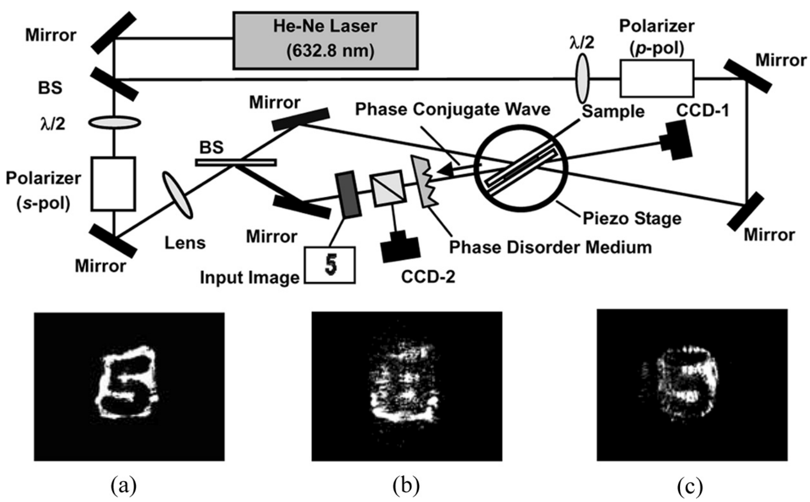

FIGURE 2 Optical phase conjugation experimental setup using a degenerated four-wave mixing (DFWM) method, and an example of image reconstruction experiment: (a) input image, (b) distorted image, and (c) phase conjugated image.

beam and tilted angle of sample, crossing angle, and beam intensity) using DFWM setup as shown in Figure 2. In this case the laser beams were expanded in diameter of 10 mm to get a large size of image.

RESULTS AND DISCUSSION

Asymmetric energy transfer between the two incident beams was observed under no electric field application as shown in Figure 3. Figure 4 indicates the NACzE concentration dependence of net 2BC gain in PMMA/NACzE system. As the amount of NACzE increases, the net gain increases dramatically and reaches a maximum ($426\,cm^{-1}$), then starts to decrease. Here, the net gain is determined as the 2BC gain subtracted the optical absorption coefficient α (Fig. 5). In the highly doped region (over PMMA/NACzE = 70:30), the optical damages such as crystallization of NACzE and degradation of optical quality were observed during the measurement. Therefore it is quite important to find the optimum concentration of guest NACzE molecules for the real application. The photorefractive characteristics for each sample were summarized in Table 1.

As easily understandable from the molecular structure of NACzE (Fig. 1), this molecule consists of carbazole unit and nitrophenyl azo unit. This implies that the carbazole unit behaves as photoconductive moiety (photocarrier generation) and the nitrophenyl azo unit behaves as NLO moiety (Pockels effect), so then NACzE seems to be a

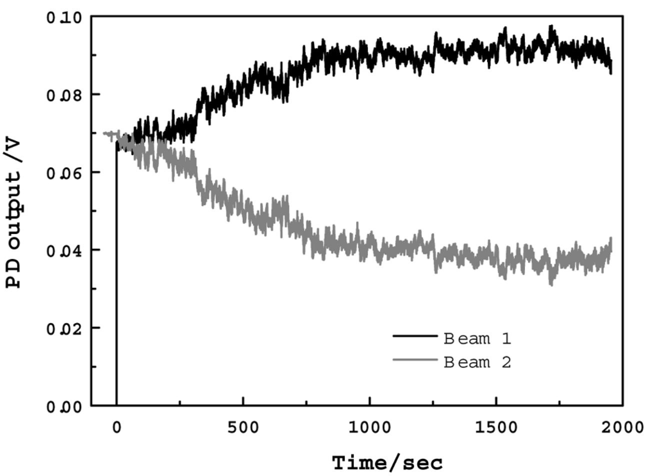

FIGURE 3 Example of asymmetric energy transfer between two beams using PMMA/NACzE (70/30) composite.

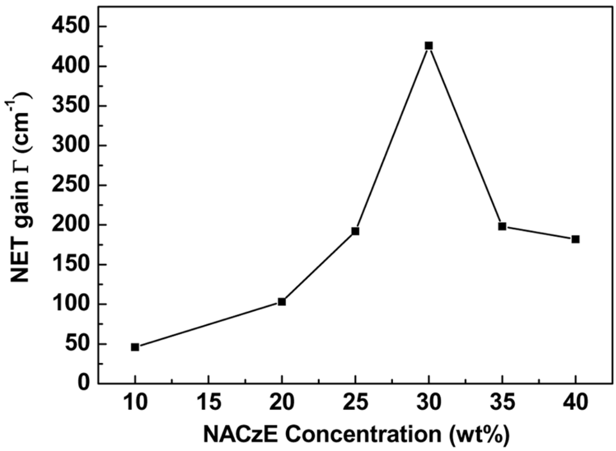

FIGURE 4 NACzE concentration dependence of net 2BC gain in PMMA/NACzE composite.

monolithic molecule. Therefore PMMA/NACzE system is a simple but promising PR composite for photorefractive application without external electric field. We are now studying the photoconductive properties of this system such as photocarrier generation efficiency and carrier mobility using a time of flight (TOF) technique.

Since the PMMA/NACzE (70:30) system has the highest value of net 2BC gain: 426 cm^{-1} and diffraction efficiency: 35%, then we performed an image processing experiment using this system in the

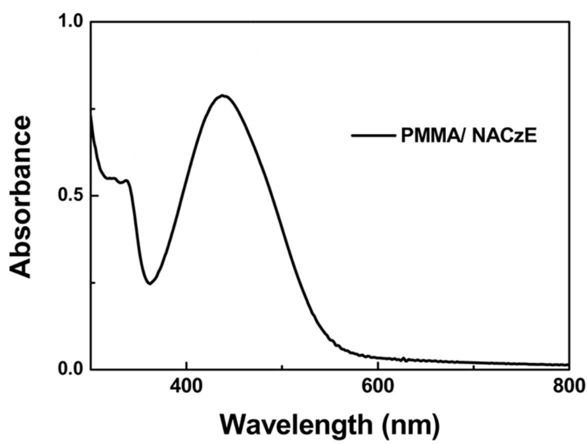

FIGURE 5 Absorption spectra of NACzE.

DFWM optical geometry. The result is shown in Figure 2: The input image (number '5' Fig. 2(a)) was distorted by the insertion of a phase distorter medium. The wave front of distorted image (Fig. 2(b)) was reconstructed via optical phase conjugation as shown in Figure 2(c). For further experiment we should check the response time of phase conjugated image formation which strongly depends on the carrier mobility in the PR film.

In addition, we prepared photorefractive composites using lower T_g polymers such as polyalkylmethacrylates (PRMA), expecting the orientational enhancement (optical poling) due to *cis-trans* isomerization of azo group in NACzE molecule. Among them we checked PEMA as a host material doped with NACzE, and observed successfully the asymmetric energy transfer under the non-electric field. Even under the non-electric field condition PEMA/NACzE (80:20) showed a net 2BC gain of $398\,cm^{-1}$ and a diffraction efficiency of 40% which is a good improvement compared to PMMA/NACzE (Table 1). Since the T_g of PEMA (63°C) is lower than that of PMMA (119°C) by 56°C, the space charge electric field formation was performed smoothly. In future we will check the T_g dependence of host polymers for the higher PR materials under non-electric field application.

CONCLUSION

We obtained high photorefractive characteristics in the NACzE doped polymer composites under non-electric field application. We successfully observed asymmetric 2BC under non-electric field: Photorefractive characteristics obtained are a net 2BC gain $(\Gamma) = 426\,cm^{-1}$ and a diffraction efficiency $(\eta) = 35\%$ for PMMA/NACzE (70:30). Furthermore, we could demonstrate its high performance by DFWM image processing experiment. The photorefractive composite using lower T_g polymer PEMA as a host material also showed the asymmetric energy transfer under the non-electric field. Photorefractive properties obtained in this system are a net 2BC gain $= 398\,cm^{-1}$ and a diffraction efficiency $= 40\%$. We will perform further studies such as an elucidation of mechanism of photorefractive effect under the non-electric field condition in future.

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