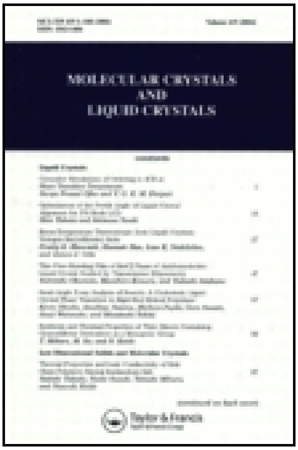

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Sep 2010

To cite this article: Jun-ichi Nishide, Akiyoshi Tanaka, Yoshiaki Hirama & Hiroyuki Sasabe (2008): Non-Electric Field Photorefractive Effect Using Polymer Composites, Molecular Crystals and Liquid Crystals, 491:1, 217-222

To link to this article: http://dx.doi.org/10.1080/15421400802330424

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 217–222, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330424

Non-Electric Field Photorefractive Effect Using Polymer Composites

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We prepared photorefractive composites using poly(3,4-ethylenedioxythiophene)-block-polyethylene glycol (PEDOT-block-PEG) as a key material doped with non-linear optical chromophore ((S)-(-)-l-(4-Nitrophenyl)-2-pyrrolidinemethanol (NPP). To adjust the optical absorbancc PMMA was used as a matrix. Photorefractive properties were characterized by means of a two beam coupling (2BC) method and a degenerated four wave mixing (DFWM) method. We successfully observed asymmetric 2BC under non-electric field: Photorefractive characteristics obtained are a net 2BC gain of 175 cm^{-1}, a diffraction efficiency of 49%, and a phase shift of 90°. Furthermore, we could demonstrate its high performance by DFWM image processing experiment.

Keywords: diffraction efficiency; image processing; net gain; non-electric field; PEDOT-*block*-PEG

INTRODUCTION

Photorefractive effect in polymer-based composites was firstly reported by Ducharme *et al.* in 1991 [1], since then it has been investigated intensively due to 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 polymeric material systems which show photorefractive effect without electric field. As reported in Ref. 8 the composite of PMMA and poly(3,4-ethylenedioxythiophene)-*block*-polyethyleneglycol(PEDOT-*block*-PEG) doped with Coumarin 6 showed a remarkable improvement of photorefractivity. We selected PEDOT-*block*-PEG as a key material in this study and ((*S*)-(-)-l-(4-nitrophenyl)-2-pyrrolidinemethanol (NPP) as a nonlinear optical chromophore. The photorefractive characteristics of polymer-based composites were evaluated by means of a two beam coupling (2BC) method and a degenerated four wave mixing (DFWM) method. In addition, we demonstrated the image reconstruction of distorted images using phase conjugation.

EXPERIMENTAL

Sample Preparation. Since a rather thick film is required for the photorefractive measurement, we used polymethylmethacrylate (PMMA) as a host material, NPP as a NLO chromophore, and *n*-butylbenzylphthalate (BBP) as a plasticizer for the thick sample preparation. These materials were dissolved in *N,N*-dimethylformamide (DMF), and then a small amount of PEDOT-*block*-PEG was doped. Materials used in this study are shown in Figure 1, and the 3 samples are summarized in Table 1. The mixed solution was casted onto an indium tin oxide (ITO)-coated glass substrate at 100°C, and then dried in nitrogen atmosphere at 100°C for 3 h. dried *in vacuo* for over night at 80°C. The film was sandwiched with another ITO-coated glass, followed by the hot press at 120°C in the nitrogen atmosphere for 10–15 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 method and DFWM method. The UV-Vis optical absorption measurement indicated that

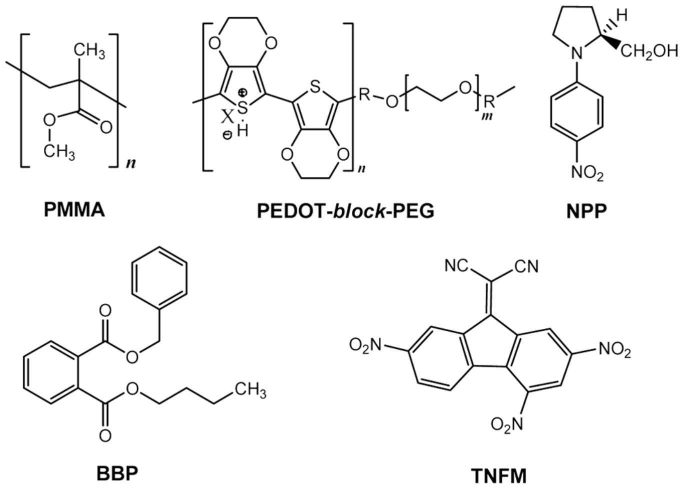

FIGURE 1 Structural formulae of chemicals used in this study.

each sample had reasonable absorption in 532 nm, then the laser wavelength was selected at 532 nm (Second Harmonic Generation of YAG: Coherent DPSS-532) 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 (51 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 11.2°, and the sample is tilted by 30° with respect to the bisector of the two writing beams. 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 $I_t(i = 1, 2)$ are the intensity of each beam/with or without the second beam, θ_1 the refraction angle of each beam and d film thickness.

TABLE 1 Composition of Samples Used in This Study

Sample 1	PMMA/NPP(20 wt%)
Sample 2	PMMA/PEDOT-*block*-PEG(2 wt%)/BBP(100 wt%)/NPP(20 wt%)
Sample 3	PMMA/PEDOT- *block*-PEG(2 wt%)/BBP(100 wt%)/NPP(50 wt%)
Sample 4	PMMA/PEDOT-*block*-PEG(2 wt%)/BBP(100 wt%)/NPP(50 wt%)/ TNFM (1 wt%)

*wt% ratio to PMMA.

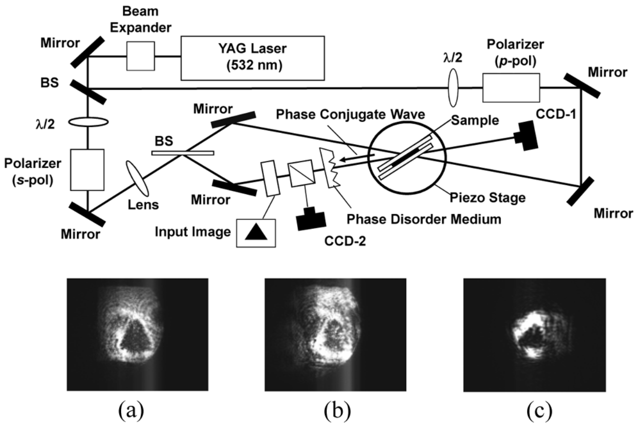

FIGURE 2 Optical phase conjugation experiments using four-wave mixing method: (a) input image; (b) distorted image; (c) phase conjugated image.

In the DFWM measurement the sample was irradiated by two *s*-polarized beams (51 mW/cm^2) of wavelength 532 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:

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

where $I_{incident}$ and $I_{different}$ 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 beam and tilted angle of sample, crossing angle, and beam intensity) using DFWM setup as shown in Figure 2.

RESULTS AND DISCUSSION

An asymmetric energy transfer between the two incident beams was observed under non-electric field. The photorefractive responses were summarized in Table 2.

The 2BC gain of PEDOT-*block*-PEG-doped composites (Sample 2) was improved remarkably compared to the no PEDOT-*block*-PEG composites (Sample 1). However. it should be noted that Sample 1 showed an asymmetric energy transfer even though it is composed of only PMMA and NPP. The origin of photorefractive effect depends

TABLE 2 Photorefractive Characteristics of Each Sample

	Absorption coefficient (α)	Phase shift (deg)	2BC gain (cm^{-1})	Net 2BC gain (cm^{-1})	Diffraction efficiency (%)
Sample 1	20	90	37	17	—
Sample 2	20	90	109	89	23
Sample 3	23	90	198	175	49
Sample 4	44	90	288	244	—

on the photocarrier generation under the light illumination (photoconductive property) followed by the second nonlinear optical effect (known as Pockels effect), so that the asymmetric energy transfer occurs between two incident beams. That is, the interference pattern formed by two beams generates the refractive index grating in the photorefractive medium due to the local electric field formation and hence the local refractive index change is caused by Pockels effect. In this sense Sample 1 looks like photoconductively inactive, and it is unexplainable the photorefractive effect in Sample 1. This result suggests that NPP is not only an NLO chromophore but slightly photoconductive (photocarrier generation and transport). Now we check the photoconductive properties of NPP under photoillumination and the carrier mobility by means of time-of-flight (TOF) measurement.

In Sample 2 small amount of PBDOT-*block*-PEG was doped, and it may enhance the carrier transport, because PEDOT is known as a

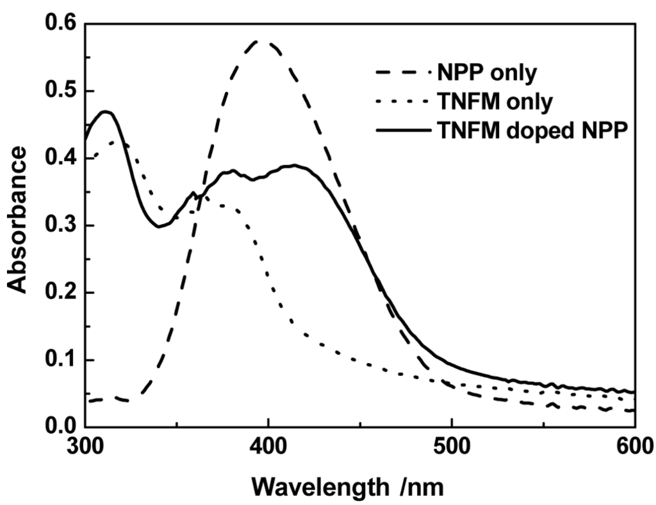

FIGURE 3 Absorption spectra of NPP, TNFM and TNFM-doped NPP.

conducting polymer. In Sample 3 the amount of NPP doped was increased, which led the increase of 2BC gain: 198 cm^{-1} and diffraction efficiency: 49%, and so we performed an image processing experiment using sample 3 as shown in Figure 2. The input image (Fig. 2(a)) was distorted by the insertion of a phase disorter medium. The wave front of distorted image (Fig. 2(b)) was reconstructed via optical phase conjugation as shown in Figure 2 (c).

For further improvement of photorefractivity, we doped (2,7,4-trinitro-9-fluorenylidene)malononitrile (TNFM) as a photosensitizer, that is to enhance the carrier generation, to Sample 3. Even under the non-electric field condition Sample 4 showed net 2BC gain of 244 cm^{-1}, which is a marked improvement compared to Sample 3 (Table 2). As shown in Figure 3, the absorption band of NPP/TNFM mixture increased in the long wavelength region. This result suggests that NPP and TNFM formed a charge transfer complex.

CONCLUSION

We obtained high photorefractive characteristics in the PEDOT-*block*-PBG doped composites under non-electric field application, and demonstrated the image processing experiment with high performance. By additional doping of TNFM to the polymer composites we obtained a considerable enhancement of net 2BC gain: 244 cm^{-1}. 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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