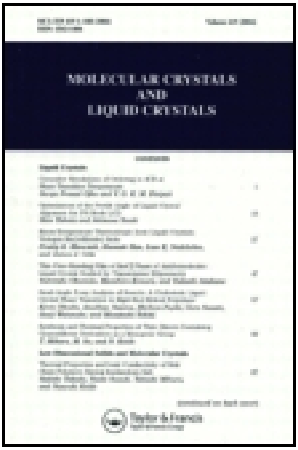

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Organic Photorefractive Composites Based on PEDOT-co-PEG

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We prepared photorefractive composites using poly(3,4-ethylenedioxythiophene)-co-poly(ethyleneglycol) (PEDOT-co-PEG) as a key material doped with nonlinear optical chromophore (Coumarin 6). To adjust the optical absorbance 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 obtained a net 2BC gain of 146 cm^{-1}, a diffraction efficiency of 9 %, a phase shift of 70° for PMMA/ PEDOT-co-PEG/ Coumarin 6/composite (Sample 2). These results were dramatically larger than traditional polyvinylcarbazole (PVCz) matrix systems.

Keywords: diffraction efficiency; net gain; PEDOT; two beam coupling

INTRODUCTION

Since the first report on photorefractive effect in inorganic electrooptic $LiNbO_3$ crystal [1], it has been intensively studied especially for the application of high density optical data storage, optical image processing, dynamic hologram, optical computing and phase conjugated mirrors. The fundamental process of photorefractive effect is well explained by the mechanism of space charge induced refractive index change in the material due to Pokels effect (second order nonlinear optical response), therefore, the requirement for photorefractive materials is summarized as follows: the material should be both

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photoconductive and NLO active under photoexcitation because it is required to generate photocarriers and to form space charge field (internal electric field: E_{int}), and then to induce a local refractive index change due to Pokels effect. The photorefractive effect has now been observed in a large number of inorganic materials such as ferroelectric crystals and semiconductors (GaAs, InP:Fe).

In 1990 the Günter's group at ETH firstly reported the photorefractive effect in an organic doped crystal [2], and then the IBM group reported the amorphous polymeric systems based on a guest-host composite in 1991 [3]. The most relevant report was issued by the Peyghambarian's group at OSC/Arizona in 1994 [4], in which they claimed a nearly 100% of diffraction efficiency and a net 2BC (two beam coupling) gain more than $200\,\mathrm{cm}^{-1}$ in the polyvinylcarbazole (PVCz) based multicomponent system. The problems were the poor optical stability due to crystallization and phase separation. After this report various candidates for organic photorefractive materials to suppress these problems have been proposed, however, still we cannot reach practical uses as yet. Among them the proposal of '*monolithic* photorefractive molecules' from the RIKEN group [5–7] was most promising but still far from the real application.

In this paper, we focused on a new composite system based on conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) copolymerized with ethylene glycol (PEG) (*i.e.*, PEDOT-*co*-PEG) to show high performance photorefractivity. It should be noted that PEDOT is used widely in various fields such as organic light-emitting diodes (OLED) and organic solar cells and PEDOT-*co*-PEG [8] is conductive (0.4 S/cm) and soluble for organic solvents.

EXPERIMENTAL

Sample Preparation: PEDOT-*co*-PEG was purchased from Aldrich and used without further purification. Since a rather thick film is required for the photorefractive measurement, we used polymethylmethacrylate (PMMA) as a host material which is also important to adjust an optical absorbance of the film; if the film has a large optical absorbance, then the photorefractive response (*e.g.*, a net two beam coupling (2BC) gain) is strongly suppressed. A small amount of PEDOT-*co*-PEG was mixed with PMMA/DMF solution, and then NLO chromophore Coumarin 6 was doped. We prepared 3 samples with different ratio of PMMA/PEDOT-*co*-PEG/Coumarin 6. As a reference we also prepared PVCz/TNF/ECz/Coumarin 6 sample (Sample 4) which is a typical photorefractive composite. Materials used in this study are shown in Figure 1, and the 4 samples are summarized in Table 1.

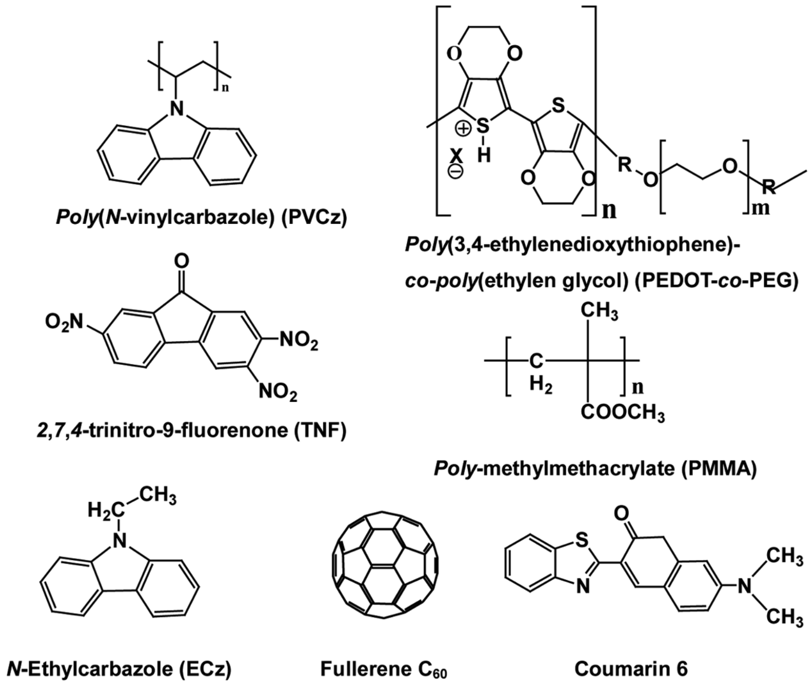

FIGURE 1 Structural formulae of chemicals used in this study.

The mixed solution was casted onto ITO glass, and then dried *in vacuo* for over night at 120°C. The film was sandwiched with another ITO glass, followed by the hot press at 100°C in the nitrogen atmosphere. Here, the film thickness was controlled by using a 50 μm-thick polyimide spacer. Finally, the film was poled at 110°C for 30 min (60 V/μm). The glass transition temperature of these samples was obtained *ca*. 99°C for PEDOT systems and 88°C for PVCz system using differential scanning calorimetry (DSC).

Photorefractive Measurements: Photorefractive properties of these samples were characterized by means of a two beam coupling (2BC)

TABLE 1 Composition of Samples Used in this Study

Sample 1	PMMA/PEDOT-*co*-PEG(2 wt%)/Coumarin 6(5 wt%)
Sample 2	PMMA/PEDOT-*co*-PEG(2 wt%)/Coumarin 6(10 wt%)
Sample 3	PMMA/PEDOT-*co*-PEG(2 wt%)/Coumarin 6(5 wt%)/ C_{60}(0.5 wt%)
Sample 4	PVCz/TNF(1 wt%)/ECz(40 wt%)/Coumarin 6(5 wt%)

*wt% ratio to PMMA and PVCz.

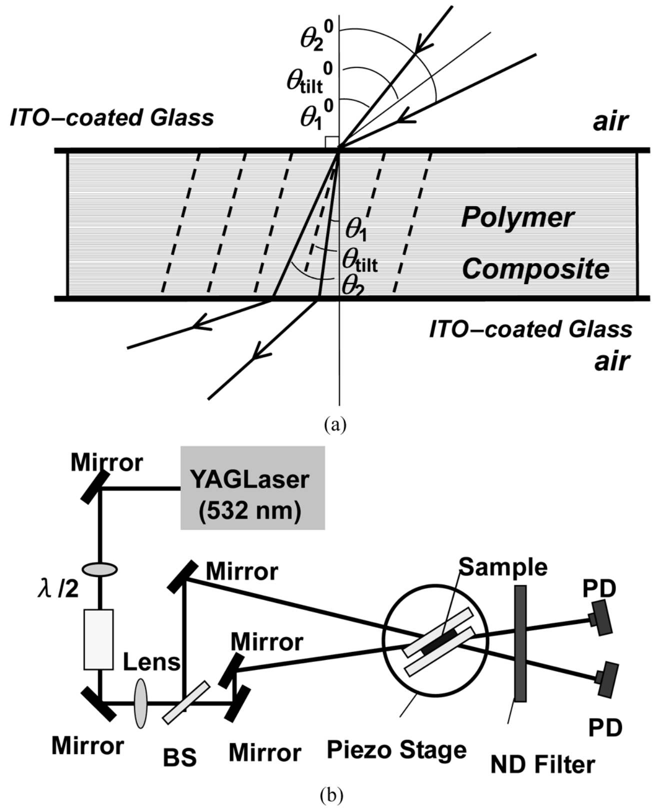

FIGURE 2 Experimental setup for Two Beam Coupling (2BC) method. (a) Beam geometry and (b) Measuring system.

method (Fig. 2) and a degenerated four wave mixing (DFWM) method (Fig. 3). It should be noted that no external electric field was applied during these measurements. As shown in Figure 2 the two *p*-polarized beams (light intensity 200 mW/cm^2) were crossed in the sample set on the piezoelectric stage. The transmitted beams after 7 min irradiation were detected by photodiodes. Here, the crossing angle between two beams was set at 11.5°.

RESULTS AND DISCUSSION

The UV-Vis optical absorption measurement indicated that each sample had reasonable absorption in 532 nm, then the laser wavelength was selected at 532 nm (Second Harmonic Generation of

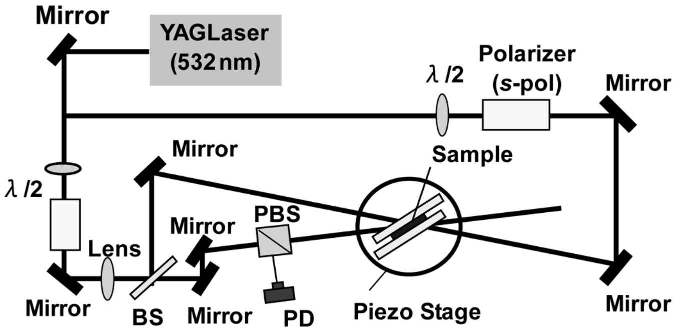

FIGURE 3 Experimental setup for Degenerated Four Wave Mixing (DFWM) method.

YAG: Coherent DPSS-532) for 2BC and DFWM measurements. From the 2BC measurement, we can calculate the 2BC gain (Γ) as follows:

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

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 (200 mW/cm^2) of wavelength 532 nm to form the grating, and irradiated one *p*-polarized beam (22 mW/cm^2). Then the diffracted beam was detected by a photodiode. The diffraction efficiency (η) is calculated as follows:

$$\eta = \frac{I_{diffract}}{I_{incident}} \quad (2)$$

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.

An asymmetric energy transfer between the two beams was observed as shown in Figure 4. The photorefractive responses were summarized in Table 2. The 2BC gain of PMMA/PEDOT-*co*-PEG/Coumarin6 and PVCz/TNF/ECz/Coumarin 6 systems were well defined, however, the net 2BC gain ($\Gamma - \alpha$) became negative in the case of PVCz system, that is, the optical absorbance (absorption coefficient α) exceeds the 2BC gain. In the former report [9] we showed a small net gain for PVCz/TNF/ECz/DO3 (disperse orange 3) system, so this result indicates that the selection of NLO chromophore is one of the

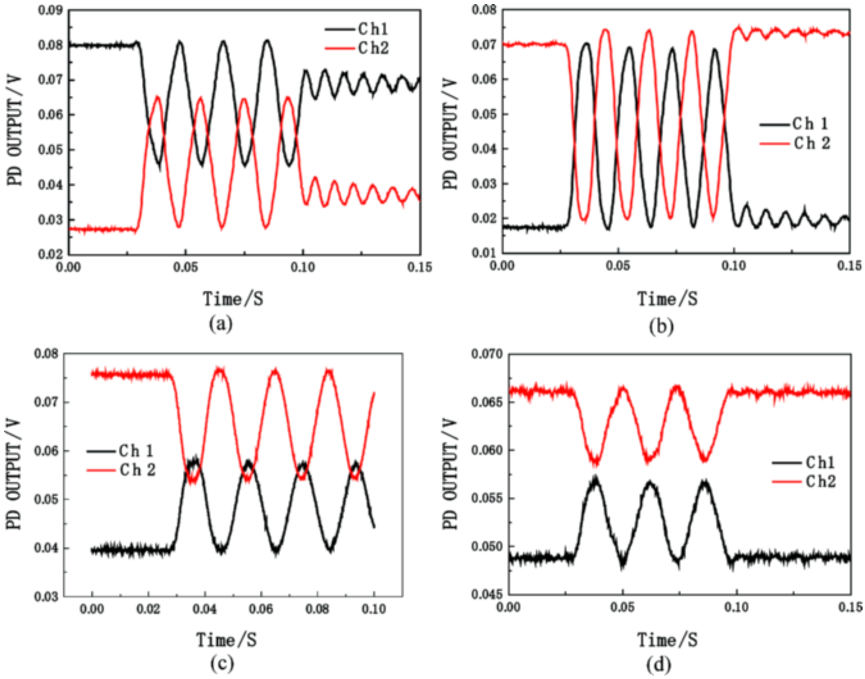

FIGURE 4 Asymmetric energy transfer between two beams at wavelength of 532 nm. (a) Sample1, (b) Sample 2, (c) Sample 3, and (d) Sample 4.

key factors to enhance photorefractive properties. Sample 3 also shows a negative net gain because of small 2BC gain against our expectation to enhance the photoconductivity by C_{60} (acceptor) doping. Increasing the NLO chromophore (Coumarin 6) concentration, the net gain increases. Since α also increases, however, there might be an optimum concentration. These results suggest that PMMA/PEDOT-*co*-PEG/ Coumarin 6 system shows dramatically large photorefractive

TABLE 2 Photorefractive Properties of Each Sample

	Phase shift (deg)	Absorption coefficient (α)	2BC gain (cm^{-1})	Net 2BC gain (cm^{-1})
Sample 1	90	57	124	67
Sample 2	70	112	258	146
Sample 3	90	83	81	—
Sample 4	63	25	15	—

responses compared with typical PVCz composites. The value of net 2BC gain reaches 146 cm^{-1} in PEDOT composite systems, which is large enough to the commercial application.

The diffraction efficiency of PMMA/PEDOT-*co*-PEG/Coumarin 6 system is 9 % so far, therefore it might be required to reduce the glass transition temperature of the sample and to apply an electric field during the refractive index grating formation for the orientational enhancement of photorefractivity. This system also has a pretty good stability: it keeps the optical quality for 3 months without any crystallization and/or phase separation.

CONCLUSION

We prepared photorefractive composites using PEDOT-*co*-PEG as a key material (photoconductor) doped with NLO chromophore (Coumarin 6). PMMA was used as a matrix to adjust optical quality and to make ease to form thick film. The PMMA/PEDOT-*co*-PEG/Coumarin 6 system showed a large net 2BC gain of 146 cm^{-1}, but small diffraction efficiency. It is required to enhance the diffraction efficiency for the real device application. For comparison we checked the PMMA/Coumarin 6 composite, but this system showed no photorefractive response. This result indicates the importance of PEDOT for the photocarrier generation, so we should optimize the PEDOT concentration in PMMA/PEDOT-*co*-PEG/Coumarin 6 system. We will check the carrier generation and transport in PMMA/PEDOT-*co*-PEG/Coumarin 6 system by means of a time of flight method in future.

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