Synthesis, Fabrication and Characterization of Photorefractive Composite Utilizing Flexible NLO Chromophores and Crosslinkable Photoconducting Matrix

Sang Chul Suh,[a] Sang Chul Shim,[a] Ae Rhan Kim,[b] and Dong Jin Yoo[c],*

[a]Department of Chemistry, Korea Advanced Institute of Science and Technology 373-1,
Guseong-Dong, Yuseong-Gu, Daejon 305-701, Korea
[b]Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea
[c]Department of Chemistry, Seonam University, 720 Gwangchi-Dong, Namwon-Si,
Chonbuk 590-711, Korea

The photorefractive composites fabricated by blending NLO chromophores such as 3-(4-{bis-[4-(2-ethylhexyloxy)-phenyl]-amino}-phenyl)-2-isocyano-acrylonitrile (PAIA), bis-[4-(2-ethyl-hexyloxy)-phenyl]-{4-[2-(4-nitrophenyl)-vinyl]-phenyl}-amine (PNPA) with photoconducting crosslinkable matrix, bis-(4-ethynylphenyl)-(4-octyloxyphenyl)-amine (BEOPEA), showed photorefractive property due to the high composition of NLO chromophores caused by introducing alkoxy chain, and many problems faced in typical organic photorefractive systems such as time-consuming chemical synthesis, difficulty in rational design, intrinsic instability and phase separation could be avoided.

Key words: photorefractivity; crosslinking; composite; photoconducting matrix; NLO chromophores

INTRODUCTION

Organic photorefractive (PR) materials are multifunctional materials that combine photoconductivity and electro-optic response to show new phenomenon: light induced reversible modulation of the refractive index [1].

In recent years, photoconducting polymers doped with electro-optical (EO) chromophores and a small amount of charge generator have shown excellent PR properties such as large two beam coupling optical gain and high diffraction efficiency [2-4]. However, this type of composite encounters inherent problems such as aggregation and crystallization of EO chromophores limiting the durability of PR devices.

To overcome these problems, monolithic PR materials have been designed, for example, fully functionalized polymers [5-8] and multifunctional low molecular weight compounds [9-11]. Fully functionalized polymers are consisted of charge transporting moieties and EO chromophores. However, they show disadvantages of time consuming chemical synthesis and poor PR properties. Most of the reported multifunctional low molecular weight compounds are molecularly dispersed in an inert polymer for efficient photorefractivity and resulting systems have low T_g and it is easy to fabricate thick film devices [9,10]. However, low T_g photorefractive devices can not be used for the optical memory applications because of the random orientation of EO chromophores without external electric field.

In this study, we report on the photorefractivity of newly designed composites having crosslinkable photoconducting triphenylamine derivatives as a matrix and amorphous NLO chromophores containing alkoxy chain to overcome many serious problems such as intrinsic instability, phase separation, difficulty in rational design and thick film preparation that are faced in the typical organic photorefractive materials.

MATERIALS AND METHODS

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 and Bruker AM-300 spectrometers and chemical shifts were reported in ppm units with TMS or the solvent CDCl$_3$ as an internal standard. A Shimadzu UV-3100S spectrophotometer was used for UV-visible spectral data. High-resolution mass spectra were determined with JEOL JMS-DX 303 mass spectrometer. The tilted geometry was used with two beams, mutually coherent beams from an NEC GLS-5404 He-Ne laser operating at a wavelength of 633 nm. Diffraction of transmitted beam intensities was monitored with photodiodes (Hamamatsu Photonics, S2281).

Materials

2-Methyl-3-butyn-2-ol, 4-iodophenol, 1-octanol, triphenylamine, copper(I) iodide, bis (triphenylphosphine)palladium(II) chloride, triphenylphospine, diphenylamine, diethyl azodicarboxylate (DEAD), electrolytic copper powder, anhydrous potassium carbonate, 18-crown-6, potassium iodide, iodic acid, POCl$_3$,

4-nitrophenylacetic acid and malonitrile were obtained commercially from Aldrich Chemical Co. and used without further purification. All solvents were carefully purified by standard methods [12].

Synthesis

Bis-(4-ethynylphenyl)-(4-octyloxyphenyl)-amine (BEOPEA) and *{4-[2-(4-nitro-phenyl)-vinyl]-phenyl}-diphenylamine* (NVPDA) were prepared according to the literature methods (Scheme 1) [16].

1-(2-Ethylhexyloxy)-4-iodobenzene (1). 4-Iodophenol (8.80 g, 40.0 mmol) and potassium carbonate (13.8 g, 100 mmol) in acetone were added to 3-bromomethyl-heptane (8.50 mL, 48.0 mmol) and refluxed. After 24 h, the solution was poured into water, extracted with ether three times and dried with anhydrous MgSO₄ and then the solution was filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with an eluent of n-hexane/ethyl acetate (50:1, v/v) to yield the liquid product **1** in 87% yield. ¹H NMR (CDCl₃, ppm) δ 0.95 (t, 6H, 2CH₃), 1.36-1.55 (m, 8H, -CH₂-), 1.71-1.75 (m, 1H, -CH-), 3.81 (d, 2H, CH₂-O-), 6.69 (d, 2H, ArH), 7.54 (d, 2H, ArH); ¹³C NMR (CDCl₃, ppm) δ 11.5, 14.5, 23.5, 24.3, 29.5, 31.0, 39.9, 71.2, 91.2, 113.4, 138.0, 158.2.

Bis-[4-(2-ethylhexyloxy)-phenyl]-phenylamine (2). Distilled aniline (1.78 mL, 19.5 mmol), 1-(2-ethylhexyloxy)-4-iodobenzene (14.4 g, 43.3 mmol), electrolytic copper powder (4.83 g, 76.0 mmol), anhydrous potassium carbonate (20.3 g, 147 mmol) and 18-crown-6 (1.00 g, 3.90 mmol) were refluxed in 1,2-dichlorobenzene (50 mL) under nitrogen until aniline disappears, as verified by TLC. After 2 days, the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was purified by passing through a very short column and by silica gel column chromatography with an eluent of n-hexane/ethyl acetate (40:1, v/v) to yield the product **2** in 67% yield. ¹H NMR (CDCl₃, ppm) δ 0.95 (t, 12H, -CH₃), 1.36-1.55 (m, 16H, -CH₂-), 1.71-1.75 (m, 2H, -CH-), 3.81 (d, 4H, CH₂-O-), 6.85 (d, 4H, ArH), 6.90 (d, 2H, ArH), 7.03 (d, 4H, ArH), 7.17 (m, 1H, ArH), 7.46 (d, 2H, ArH); ¹³C NMR

(CDCl₃, ppm) δ 11.5, 14.5, 23.5, 24.3, 29.5, 31.0, 39.9, 71.2, 115.7, 126.8, 128.1, 129.3, 130.9, 141.4, 149.3, 156.0.

4-{Bis-[4-(2-ethylhexyloxy)-phenyl]-amino}-benzaldehyde (3). POCl₃ (0.73 mL, 7.80 mmol) was slowly added to a stirred solution of bis-[4-(2-ethylhexyloxy)-phenyl]-phenyl-amine (3.74 g, 7.67 mmol) and dimethylformamide (0.6 mL, 7.8 mmol) in 50 mL of 1,2-dichloroehane. Subsequently the solution was refluxed for 2 h, cooled, and poured into water. The resulting mixture was extracted with dichloromethane. After drying with MgSO₄, the solvent together with the 1,2-dichloroethane and DMF was removed by evaporation under reduced pressure. The crude product was purified by silica gel column chromatography using n-hexane/ethyl acetate (10:1, v/v) as the eluent, to obtain the product **3** in 83% yield. ¹H NMR (CDCl₃, ppm) δ 0.95 (t, 12H, -CH₃), 1.36-1.55 (m, 16H, -CH₂-), 1.71-1.75 (m, 2H, -CH-), 3.81 (d, 4H, CH₂-O-), 6.79 (d, 4H, ArH), 6.85 (d, 2H, ArH), 7.09 (d, 4H, ArH), 7.57 (d, 2H, ArH), 9.92 (s, 1H, -CHO); ¹³C NMR (CDCl₃, ppm) δ 11.5, 14.5, 23.5, 24.3, 29.5, 31.0, 39.9, 71.2, 115.7, 128.6, 129.0, 132.1, 132.6, 139.6, 155.1, 158.5, 190.0.

Bis-[4-(2-ethylhexyloxy)-phenyl]-{4-[2-(4-nitrophenyl)-vinyl]-phenyl}-amine (PNPA). In a 500 mL three-neck flask fitted with mechanical stirrer and condenser was added 4-nitro-phenylacetic acid (1.47 g, 8.11 mmol) and piperidine (1.60 mL, 16.2 mmol) was added, followed by the addition of 4-{bis-[4-(2-ethylhexyloxy)-phenyl]-amino}-benzaldehyde (3.86 g, 7.70 mmol) in 200 mL of ethanol. The resultant mixture was refluxed for 5 h and cooled. Then 20 mL of ethanol was added to the mixture, filtered, washed, and vacuum dried. The crude product was finally purified by using column chromatography n-hexane/ethyl acetate (10:1, v/v) to yield the product (PNPA) in 62% yield. ¹³C NMR (CDCl₃, ppm) δ 114.8, 116.1, 123.1, 125.3, 126.7, 126.8, 128.5, 128.9, 129.8, 130.1, 144.7, 147.6, 150.6, 158.1; HRMS (M⁺) calcd for C₄₂H₅₂N₂O₄ 648.3927, found 648. 3934.

3-(4-{Bis-[4-(2-ethylhexyloxy)-phenyl]-amino}-phenyl)-2-isocyanoacrylonitrile (PAIA). A solution containing 4-{bis-[4-(2-ethylhexyloxy)-phenyl]-amino}-benzaldehyde in 50 mL of ethanol was added malonitrile (0.46 g, 7.0 mmol) and a catalytic amount of 0.1 M NaOH solution. The reaction mixture was stirred for 5 h at 50°C, cooled, and poured into water. The solvent was distilled under reduced pressure and the residue was purified by silica gel column chromatography with an eluent of n-hexane/ethyl acetate (5:1, v/v) to yield the product in 72% yield. ¹H NMR (CDCl₃, ppm) δ 0.92 (t, 12H, -CH₃), 1.36-1.52 (m, 16H, -CH₂-), 1.69-1.73 (m, 2H, -CH-), 3.81 (d, 4H, CH₂-O-), 6.79 (d, 4H, ArH), 6.89 (d, 2H, ArH), 7.10 (d, 4H, ArH), 7.44 (s, 1H, C=CH-) 7.68 (d, 2H, ArH); ¹³C NMR (CDCl₃, ppm) δ 11.5, 14.5, 23.5, 24.3, 29.5, 31.0, 39.9, 71.2, 114.8, 115.9, 116.0, 116.1, 116.9, 122.0, 128.5, 133.5, 137.8, 154.6, 158.1, 158.2; HRMS (M⁺) calcd for C₃₈H₄₇N₃O₂ 577.3668, found 577.3664 (Scheme 2).

Preparation of composites and devices

C₆₀
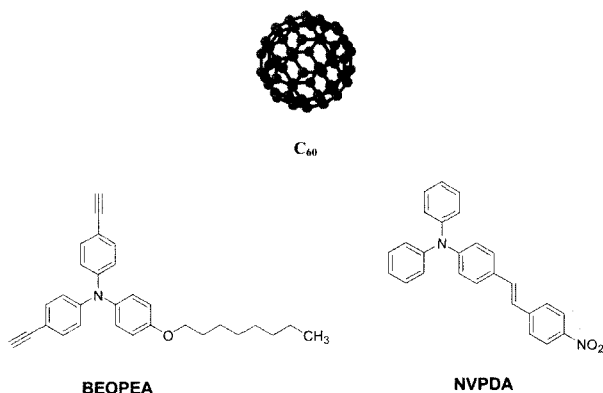
BEOPEA   NVPDA

Scheme 1. Chemical structures of BEOPEA, NVPDA and C₆₀.
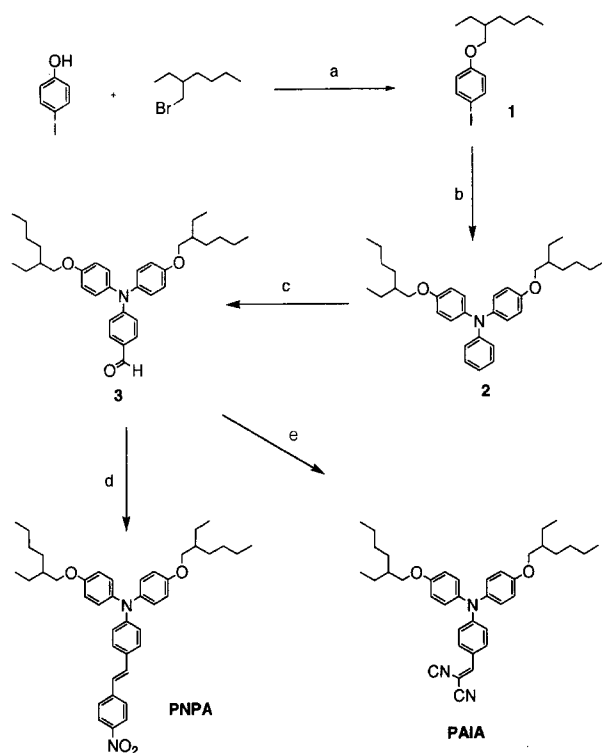
Scheme 2. Synthetic procedures of PNPA and PAIA. (a) K_2CO_3, acetone, reflux, 24 h; (b) Aniline, Cu, K_2CO_3, 18-crown-6, ODCB, reflux, 48 h; (c) $POCl_3$, DMF, 1,2-dichloroethane, reflux, 2 h; (d) 4-Nitrophenylacetic acid, piperidine, EtOH, reflux, 5 h; (e) $CH_2(CN)_2$, NaOH, EtOH, 50°C, 5 h.
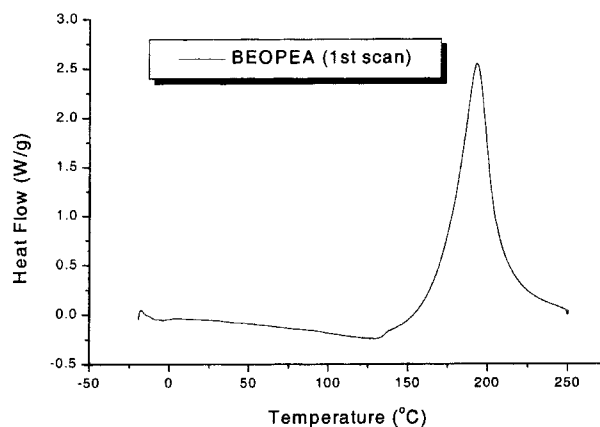

Figure 1. The differential scanning calorimeter (DSC) curve of BEOPEA; exothermal reaction starts at about 130°C.

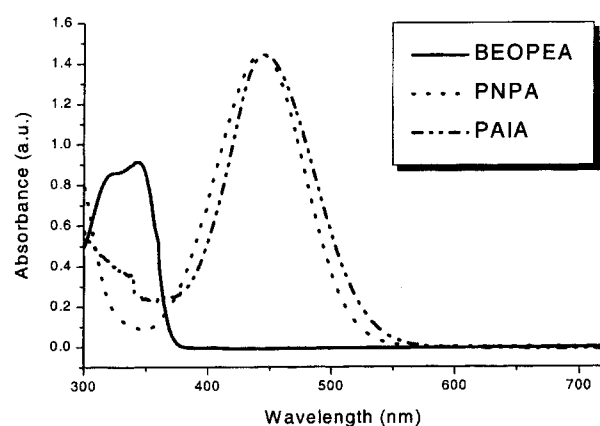Figure 2. The UV-vis absorption spectra of BEOPEA, PNPA and PAIA.

The photorefractive properties of the various composites were studied by the four-wave mixing (FWM) and two-beam coupling (2BC) techniques for the 100 mm thick films sandwiched between two indium-tin-oxide covered glasses. Each composite was doped with 1 wt % of C_{60} as a charge generator. The composition was monitored by varying the amount of NLO chromophore. The device was poled with a dc electric field (5 KV) for 30 min and that was heated, in vacuum and in the dark, on a hot-stage from room temperature up to 80°C. The acetylene moiety in BEOPEA was crosslinked at this temperature and that phenomenon was monitored by DSC curve as shown in Figure 1. The device was held at this temperature for 30 min and then cooled to 30-40°C for 30 min under the electric field.

RESULTS AND DISCUSSION

The synthesis of BEOPEA, photoconducting and cross-linkable matrix, in photorefractive composite was described in the previous literature [6] and bifunctional molecules which have nonlinear optical and photoconducting properties, PAIA and PNPA, were synthesized in four steps using alkylation, Ullman reaction, formylation and Michael type addition as described in Scheme 2. Each product shows amorphous, sticky state at room temperature and has relatively high

solubility in organic solvents such as toluene, chloroform and methylene chloride, which facilitates spectroscopic characterization by NMR, HRMS (M^+) methods.

The inset in Figure 2 shows the UV absorption spectra of BEOPEA, PAIA and PNPA. The important feature of an organic photorefractive system is its absorption spectrum, since this determines the wavelength region in which the material can be used. It is clear that NLO chromophore should not absorb the light source in the wavelength region of interest and not much overlap with the absorption of photoconducting matrix [13,14]. The absorptions at 445 nm and 448 nm are due to the PAIA, PNPA respectively and that at 345 and 323 nm is due to the BEOPEA showing not much overlap with the NLO chromophore absorption region. These spectra were almost the same as those obtained by superimposing the spectrum of each unit. Therefore, it is considered that no electrical interactions exist, at least in the ground state between the TPA unit and NLO chromophore. The absorption coefficient above 600 nm is very low and is almost likely due to the charge-transfer complex with C_{60}. Therefore, the photorefractive characterizations can safely be performed using a

He-Ne laser which emits at 633 nm.

We introduced thermally crosslinkable functional group into the hole transporting triphenylamine (TPA) derivatives and the T_g of the composite is lowered by connecting flexible alkyl chains. Softening the composite by flexible chains and stabilization by crosslinking will make the fabrication of thick photo-refractive film easier and also will give a long-term stability of the orientation of NLO chromophores. The photorefractive properties of the BEOPEA/NVPDA/C_{60} composite have been studied previously in our goup [16]. The photorefractive properties were monitored by varying the amount of NLO chromophore such as 89/10/1 and 64/35/1, and the composite containing more NLO chromophore composition (35 wt%) gave better optical gain and diffraction efficiency corresponding with theoretical results [16]. Therefore, we tried to increase the concentration of NLO chromophores to improve the photo-refractive properties. However, the higher the ratio of the NLO composition, the higher the T_g of the composite was observed which is not feasible for the easy preparation of thick film devices. We, therefore, introduced flexible alkoxy chains to the NLO chromophores to lower the T_g of the composite, and to improve the photorefractive properties such as two beam coupling gain and four wave mixing diffraction efficiency effectively caused by high ratio of NLO chromophores in the composite.

All the components in the photorefractive composites were dissolved in purified toluene containing C_{60} (1 wt%) at desired concentrations. The composite solution was filtered through a 0.5-mm filter and cast onto ITO covered glass substrate at room temperature. The viscous solutions were left to evaporate residual solvent in vacuum at room temperature for 3 days and the sample were sandwiched with another ITO-covered glass. Although varying the NLO composition up to 70%, the resulting composite maintains its viscous state and did not show any aggregations or crystallization. The device was poled with a dc electric field (5 KV) for 30 min and heated in vacuum in the dark on a hot-stage from room temperature up to the 80°C. The acetylene moiety in BEOPEA was crosslinked at this temperature as monitored by DSC. The device was held at this temperature for 30 min and then cooled to 30-40°C for 30 min under the electric field. As the crosslinking reaction proceeded, the network-like structure is formed and the NLO chromophore oriented by the external electric field is fixed. The composite did not solve any solvent, and UV-absorption pattern changed not much after crosslinking reaction.

The FWM diffraction efficiency for different samples containing five NLO chromphore concentrations was measured as a function of the applied electric field as shown in Figure 3 and 4. Holographic gratings were written using two mutually coherent beams from a He-Ne laser operating at 633 nm. Two writing beams were s polarized, and had a power of 200 mW/cm^2 each intersecting in the sample at incidence angles of $\theta = 45°$ and $\theta = 62°$. The reading beam was p polarized and had a
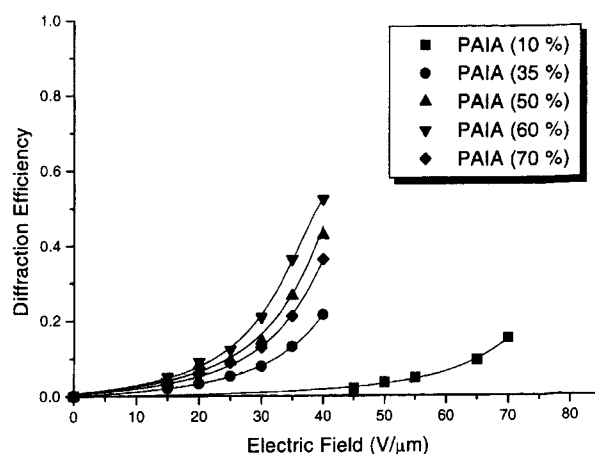

Figure 3. Electric field dependence of the four wave mixing diffraction efficiency varying the concentrations of PAIA.
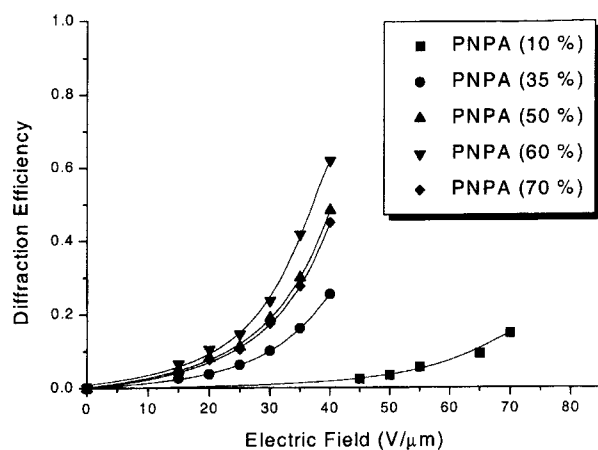

Figure 4. Electric field dependence of the four wave mixing diffraction efficiency varying the concentrations of PNPA.

power of 8 mW/cm^2. In the case of NVPDA doped composite, a maximum diffraction efficiency (29%) was observed at an applied electric field of 42 V/μm for 35 wt% NLO chromophore doped sample [16]. The newly synthesized NLO chromophore, PNPA, having the same structure with NVPDA except alkoxy chain was introduced to the composite varying compositions such as 10 wt%, 35 wt%, 50 wt%, 60 wt% and 70 wt% to optimize the condition and resulting composite shows higher diffraction efficiency up to 57.2% at 40 V/μm than the composite containing NVPDA due to the higher concentration of NLO chromophore (Figure 4). The PAIA doped composite shows lower diffraction efficiency such as 49.3 % at 40 V/mm than PNPA contained composite caused by lower electro-optic coefficient of dicyano group [15] (Figure 5). At 70-wt% of NLO chromophore composition, the diffraction efficiency is decreased indicating that the space charge field is not effectively formed due to relatively lower concentration of the hole transporting matrix (BEOPEA).

The optical gain coefficient Γ represents the index of photorefractivity and it is related to the electro-optic (EO)
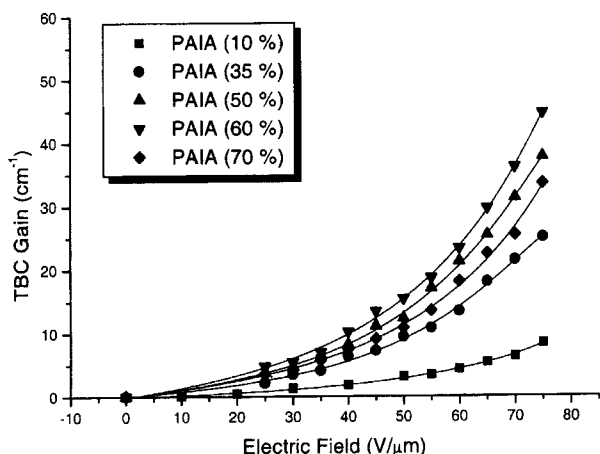
Figure 5. Electric field dependence of the two beams coupling gain varying the concentrations of PAIA.
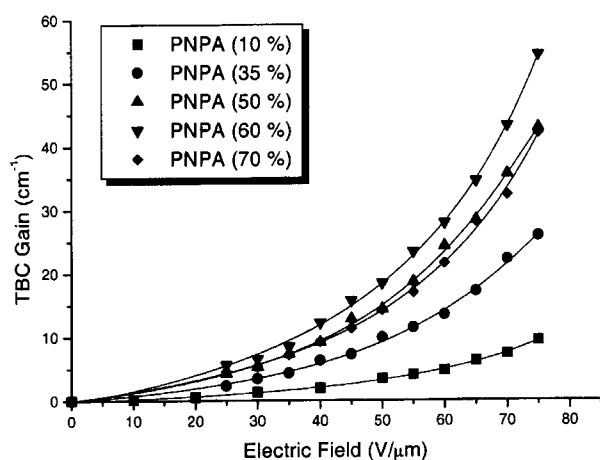

Figure 6. Electric field dependence of the two beams coupling gain varying the concentrations of PNPA.

coefficient and photoconductivity by

$$\Gamma = 2p\pi n^3 r_{eff} E_{sc}/m\lambda$$

where λ is the wavelength of the writing beam, p is a projection factor, r_{eff} is the effective EO coefficient proportioned to d_{33} value, m is the modulation depth, and E_{sc} is the space charge field related to photoconductivity. For 2BC experiments, two coherent He-Ne laser beams illuminate a photorefractive sample. They interfere in the sample and they write an index grating in the material. An asymmetrical exchange of energy between the two beams clearly indicates that resulting grating is phase shifted. The 2BC gain of the composite was calculated from the intensity changes of the first writing beam with the second writing beam being on and off. The 2BC gain was measured as a function of the applied electric field for each of the samples prepared and studied in the four-wave mixing experiments. The optical gain of PNPA, PAIA contained composites was also obtained by changing the composition of NLO chromophores, and gives the corresponding results with FWM experiments (Figure 5 and

6). The composite (BEOPEA/PNPA/C_{60}=39/60/1) and (BEOPEA/ PAIA/C_{60}=39/60/1) show maximum two beam coupling gain 54.3 cm^{-1}, 44.6 cm^{-1} at 75 V/mm in its composition ratio.

CONCLUSIONS

The composites (BEOPEA/PNPA/C_{60}) and (BEOPEA/PAIA/ C_{60}) were fabricated, and investigated the photorefractive properties such as two beam coupling optical gain and four wave mixing diffraction efficiency. We introduced cross-linkable and photoconducting TPA derivatives, BEOPEA, into the composite to make the preparation of thick film easy and fixing the orientation of NLO chromophores. To increase the composition of NLO chromophore without raising the T_g of the composite, flexible alkoxy chains are introduced into the triphenylamine moiety of NVPDA and the photorefractive properties of these composites were improved much more than the previous composite systems prepared in our laboratory.

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