

An approach to Photorefractive Device Fabrication Utilizing Crosslinking Systems[#]

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The composites fabricated by blending nonlinear optical (NLO) chromophore such as {4-[2-(4-nitrophenyl)-vinyl]phenyl}diphenylamine (NVPDA) with photoconducting crosslinkable matrix, bis-(4-ethynylphenyl)-(4-octyloxyphenyl)amine (BEOPEA), showed photorefractive property. 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 by this fabrication method.

key words: Photorefractivity, Crosslinking, Poling, Composite

INTRODUCTION

Some organic materials or polymers possess photorefractive properties comparable to their inorganic counterparts have received much attention [1]. They can largely be classified into host-guest systems [2, 3] or fully functionalized systems [4, 5]. The host-guest composite systems can be prepared and optimized very easily but they have major disadvantages such as intrinsic instability and phase separation. On the other hand, fully functionalized systems exhibit long-term stability and minimize phase separation, but show serious shortcomings such as time-consuming chemical synthesis and difficulty in rational design.

A thick film of 100 nm is necessary for fabricating photorefractive devices in the field of multifunctional organic polymeric materials. Plasticizers or matrix polymers with low glass transition temperatures (T_g) are introduced to decrease T_g for utilizing molecular reorientation [6, 7]. However, the orientation of the incorporated chromophores becomes unstable due to the low T_g . Many of the host-guest materials and low T_g multifunctional polymers known to date exhibit slow rise-time in the order of a few seconds either due to a slow build-up of the space-charge field or slow orientation of the chromophores [8].

In this study, we report on the photorefractivity of newly designed composites having crosslinkable photoconducting triphenylamine derivatives as a matrix and NLO chromophores to overcome many serious problems such as intrinsic instability, phase separation, difficulty in rational design and

thick film preparation that are faced in the many organic photorefractive materials.

MATERIALS AND METHODS

2.1. Materials

4-Iodophenol, 1-octanol, triphenylamine (TPA), triphenylphosphine, electrolytic copper powder, anhydrous potassium carbonate, 18-crown-6, potassium iodide, iodic acid were obtained commercially from Aldrich Chemical Co. Some chemicals and solvents were purified by standard methods [11]. Solvents of reagent grade were used for chromatography without further purification. A chromatography column of silica gel was prepared with Kieselgel 60 (70-230 mesh).

2.2. Preparation of BEOPEA

2.2.1. *1-Iodo-4-octyloxybenzene(1)*. 4-Iodophenol (5.0 g, 22.7 mmol), 1-octanol (4.29 mL, 27.0 mmol) and triphenylphosphine (7.08 g, 27.0 mmol) in THF were added to diethyl azodicarboxylate (DEAD) (4.25 mL, 27.0 mmol) at 0°C for 30 min, then raised the temperature up to room temperature. After 24 h, the solution was filtered, evaporated to remove THF and extracted with ether three times and dried with anhydrous $MgSO_4$ 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 (v/v, 50/1) to yield the liquid product (**1**). Yield: 93%; ¹H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $-CH_3$), 1.24-1.31 (m, 8H, $-CH_2-\times 4$), 1.42 (m, 2H, $O-CH_2-CH_2-$), 3.91 (t, 2H, CH_2-O-), 6.70 (d, 2H, PhH), 7.56 (d, 2H, PhH); ¹³C NMR (400 MHz, $CDCl_3$) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 32.2, 68.6, 91.3, 113.4, 138.1, 158.2.

2.2.2. *(4-Octyloxyphenyl)diphenylamine(2)*. Diphenylamine (2.88

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Received September 4, 2003; Accepted December 11, 2003

g, 17.0 mmol), 1-iodo-4-octyloxybenzene (6.34 g, 19.1 mmol), electrolytic copper powder (2.16 g, 34.0 mmol), anhydrous potassium carbonate (9.40 g, 68.0 mmol) and 18-crown-6 (0.45 g, 1.70 mmol) were refluxed in 1,2-dichlorobenzene (100 mL) under nitrogen until disappearance of the aniline as verified by TLC. After 3 days, the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was freed from the impurities by passing through a very short column and by silica gel column chromatography with an eluent of *n*-hexane/ethyl acetate (v/v, 20/1) to yield the product (2). Yield: 72%; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, -CH₃), 1.24-1.31 (m, 8H, -CH₂- × 4), 1.42 (m, 2H, O-CH₂-CH₂-), 3.91 (t, 2H, CH₂-O-), 6.83 (d, 4H, PhH), 6.91 (d, 2H, PhH), 7.01 (d, 4H, PhH), 7.18 (m, 1H, PhH), 7.45 (d, 2H, PhH); ¹³C NMR (400 MHz, CDCl₃) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 32.2, 68.6, 115.8, 126.7, 128.0, 129.2, 130.9, 141.4, 149.4, 156.1.

2.2.3. *Bis-(4-iodophenyl)-(4-octyloxyphenyl)amine(3)*. (4-Octyloxyphenyl)diphenylamine (7.10 g, 19.0 mmol), potassium iodide (4.20 g, 25.3 mmol) and iodic acid (2.23 g, 12.7 mmol) were refluxed in acetic acid (100 mL) under nitrogen. After 24 h, the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was freed from the impurities by passing through a very short column and by silica gel column chromatography with an eluent of *n*-hexane/ethyl acetate (v/v, 20/1) to yield the product in 95%; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, -CH₃), 1.24-1.31 (m, 8H, -CH₂- × 4), 1.42 (m, 2H, O-CH₂-CH₂-), 3.91 (t, 2H, CH₂-O-), 6.76 (d, 4H, PhH), 6.79 (d, 2H, PhH), 6.95 (d, 2H, PhH), 7.45 (d, 4H, PhH); ¹³C NMR (400 MHz, CDCl₃) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 32.2, 68.6, 115.9, 91.2, 124.5, 128.1, 138.2, 139.6, 147.0, 156.8.

2.2.4. *4-[4-[4-(3-Hydroxy-3-methylbut-1-ynyl)phenyl]-(4-octyloxyphenyl)amino]phenyl]-2-methylbut-3-yn-2-ol(4)*. 2-Methyl-3-butyn-2-ol (1.16 mL, 12.0 mmol) was added to a solution of bis(triphenylphosphine)palladium(II) chloride (280 mg, 0.399 mmol), copper(I) iodide (150 mg, 0.788 mmol), and bis-(4-iodophenyl)-(4-octyloxyphenyl)amine (2.86 g, 4.47 mmol) in triethylamine/toluene (v/v=3/2, 200 mL) under nitrogen atmosphere. The mixture was heated to 80°C and maintained at that temperature for several hours. After evaporation of solvents, the reaction mixture was extracted with ether and separated by silica gel column chromatography using *n*-hexane/ethyl acetate (v/v, 3/1) as an eluent to give the product in 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, -CH₃), 1.24-1.31 (m, 8H, -CH₂- × 4), 1.42 (m, 2H, O-CH₂-CH₂-), 1.56 (s, 12H, -CH₃- × 4), 3.91 (t, 2H, CH₂-O-), 6.79 (d, 2H, PhH), 6.87 (d, 4H, PhH), 6.95 (d, 2H, PhH), 7.22 (d, 4H, PhH); ¹³C NMR (400 MHz, CDCl₃) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 31.4, 32.2, 65.9, 68.6, 82.4, 93.6, 115.9, 116.2, 122.5, 128.1, 132.9, 139.6, 147.8, 156.8.

2.2.5. *Bis-(4-ethynylphenyl)-(4-octyloxyphenyl)amine (BEOPEA)*. The mixture of 4-[4-[4-(3-hydroxy-3-methyl-but-1-ynyl) phenyl]-(4-octyloxyphenyl)amino]phenyl]-2-methylbut-3-yn-2-ol (1.69 g,

3.14 mmol) and sodium hydroxide (314 mg, 7.85 mmol) in benzene (100 mL) was refluxed for several hours. The mixture was filtered through a silica gel column using *n*-hexane/diethyl ether (v/v, 5/1) as an eluent after extraction with diethyl ether and the solvent was removed under reduced pressure to give the product in 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, -CH₃), 1.24-1.31 (m, 8H, -CH₂- × 4), 1.42 (m, 2H, O-CH₂-CH₂-), 3.08 (s, 2H, H- ≡ × 2), 3.91 (t, 2H, CH₂-O-), 6.79 (d, 2H, PhH), 6.87 (d, 4H, PhH), 6.95 (d, 2H, PhH), 7.19 (d, 4H, PhH); ¹³C NMR (400 MHz, CDCl₃) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 32.2, 68.6, 78.4, 84.6, 115.9, 116.2, 122.5, 128.1, 132.9, 139.6, 147.8, 156.8; HRMS (M⁺) calcd for C₄₂H₅₂N₂O₄ 421.2406, found 421.2401.

2.3. Preparation of Composites and Devices

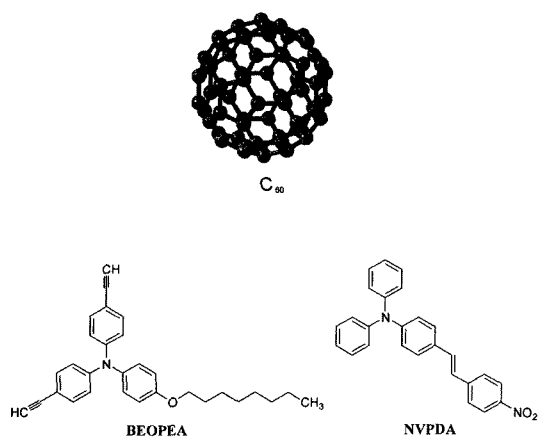
The photorefractive properties of the various composite were studied by the four-wave mixing (FWM) and two-beam coupling (2BC) techniques for the 100 μm thick films sandwiched between two indium-tin-oxide covered glasses. Each composite was prepared by doping BEOPEA/NVPDA dissolved in 1,2-dichloroethylene with 1 wt % of C₆₀ dissolved in toluene, and that the solvent was evaporated in the vacuum oven at room temperature. The device was poled with a dc electric field (5 KV) for 30 min and that was heated in vacuum on a hot-stage up to the 130°C. The acetylene moiety in BEOPEA was crosslinked at this temperature. The device was held at this temperature for 30-45 min and then cooled to 30-40°C for 30 min under the electric field.

RESULTS AND DISCUSSION

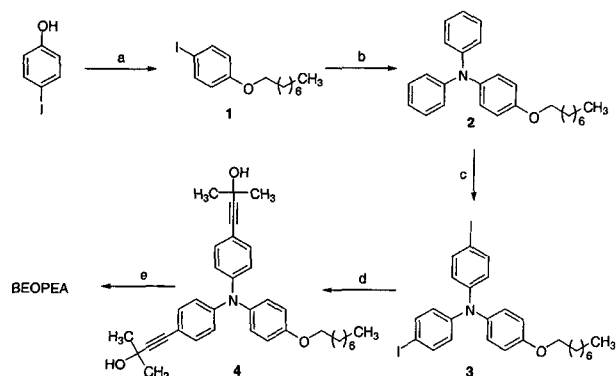
A new photorefractive composite material composed of photoconducting bis-(4-ethynylphenyl)-(4-octyloxyphenyl)amine (BEOPEA) matrix, a nonlinear optical (NLO) chromophore, {4-[2-(4-nitrophenyl)-vinyl]-phenyl}diphenylamine (NVPDA) and charge generator (CG), C₆₀ was assembled as shown in Scheme 1. BEOPEA was successfully synthesized in five steps including Mitsunobu alkylation and Ullman reaction as described in Scheme 2.

The UV absorption spectra (Figure 1) shows λ_{max} at ~445 nm due to NVPDA and peaks at 345 and 323 nm are due to the BEOPEA. The spectra are almost equal to the sum of the absorption spectrum of each unit indicating no electronic interaction between the TPA unit and NLO chromophores in the ground state. The composite has a low T_g and relatively high solubility in organic solvents such as chloroform and methylene chloride, which facilitates spectroscopic characterization by NMR and IR methods.

Triphenylamine (TPA) derivatives are good matrix and hole transporting materials. The T_g of the matrix is lowered by introducing flexible alkyl chains to make the fabrication of thick photorefractive films easy. We introduced thermally crosslinkable ethynyl group on TPA. Crosslinking of TPA matrix will give a long-term stability of the nonlinear optical



Scheme 1. Chemical structures of BEOPEA, NVPDA and C_{60} .



Scheme 2. (a) 1-Octanol, PPh_3 , DEAD, THF, $0^\circ C$, 30 min. (b) Ph_2NH , Cu powder, K_2CO_3 , 18-crown-6, 1,2-dichlorobenzene, reflux, 3 day. (c) KI, KIO_3 , AcOH, reflux, 24 hr. (d) 2-Methyl-3-butyn-2-ol, $(PPh_3)_2PdCl_2$, CuI, NEt_3 . (e) NaOH, benzene, reflux.

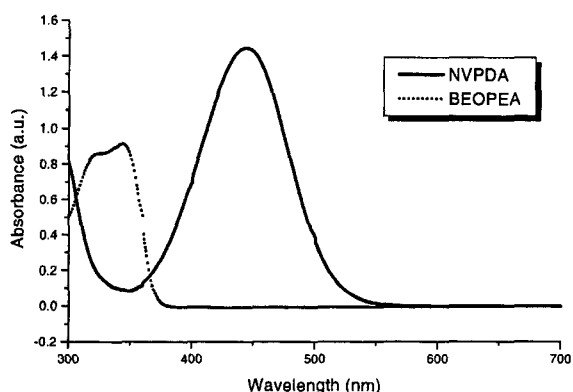


Figure 1. The UV-vis absorption spectra of BEOPEA and NVPDA.

(NLO) chromophore. The mechanism of the crosslinking reaction of ethynyl moiety was reported earlier and utilization of the crosslinking reaction enhanced the thermal stability of polymer materials in optical waveguide devices [9, 10].

The photorefractive properties of the BEOPEA/NVPDA/

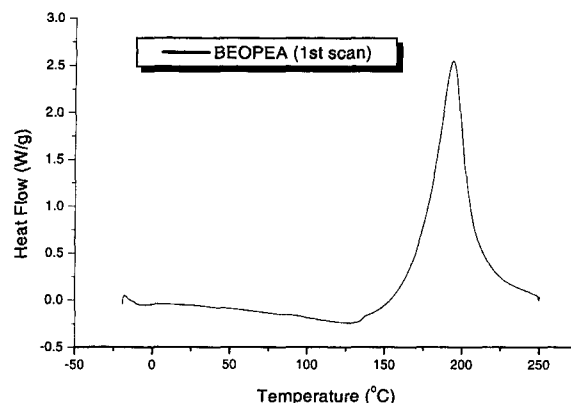


Figure 2. The differential scanning calorimeter (DSC) curve of BEOPEA; Exothermic reaction starts at about $130^\circ C$.

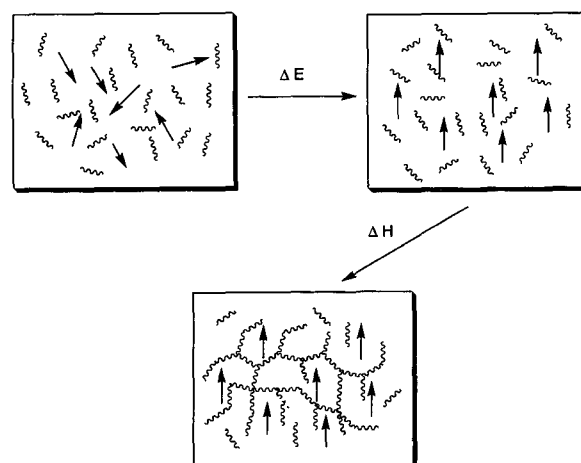


Figure 3. The effect of external electric field and crosslinking on the orientation of chromophores.

C_{60} composite were studied by the four-wave mixing (FWM) and two-beam coupling (2BC) techniques for the $100 \mu m$ 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 in such a ratio as 89/10/1 and 64/35/1. 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 $130^\circ C$. The acetylene moiety in BEOPEA was crosslinked at this temperature and the exothermic behavior was monitored by DSC as shown in Figure 2. The device was held at this temperature for 30-45 min and then cooled to $30-40^\circ C$ for 30 min under the electric field. As the electric field is introduced to the sandwich cell, the NLO chromophores, NVPDA, are directed by permanent pole and then BEOPEA matrix is crosslinked to form a network-like structure on raising the temperature (Figure 3). The thermally crosslinked devices of each composite did not show phase separation phenomenon caused by aggregation or crystallization of NLO chromophores and they were insoluble

in any organic solvent. The intensity of the UV absorption peak of the NLO chromophores (NVPDA) decreases after poling indicating that the chromophores are successfully oriented normal to the substrate plane. The decreased intensity of UV absorption peak of NLO chromophores is not much changed after several days meaning that the oriented chromophores have high stability caused by crosslinked matrix.

The FWM diffraction efficiency of samples containing two different NLO chromophore concentrations and PR growth time were measured as shown in Table 1. Holographic gratings were measured 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/cm² each intersecting in the sample at incidence angles of $\theta = 45^\circ$ and $\theta = 62^\circ$. The reading beam was *p* polarized and had a power of 8 mW/cm². The diffraction efficiency (15%) was observed at an applied electric field of 42 V/ μ m for the 35 wt% of NLO chromophore doped sample which was crosslinked at 130°C for 45 min.

For 2BC experiments, two coherent He-Ne laser beams were illuminated to a photorefractive sample. They interfere in the sample and 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. Almost the same experimental geometry as in FWM was used except *p*-polarized writing beams were utilized. The normalized beam-coupling gain coefficient Γ is given in terms of the measured quantities γ_0 and β .

$$\Gamma = [1/(d \cos\theta)] \cdot [\ln(\gamma_0 \beta) \ln(\beta + 1 - \gamma_0)]$$

Here, β is the ratio of the power of the writing beams in front of the sample, and $\gamma_0 = I/I_0$ is the beam coupling ratio where I_0 is the detected beam intensity without the pumping beam, and I is the intensity with pumping beam on, and d , θ is the sample thickness and the incident angle of the beam inside the sample, respectively. In a two-beam coupling (2BC) experiment, the energy transfer between the *p*-polarized writing beams is observed by monitoring the intensity of each of the writing beams when an external electric field is applied. Figure 4 and Figure 5 show the gain coefficient of samples

Table 1. Photorefractive properties of PR composites.

	Optical Gain	Diffraction Efficiency
BEOPEA/NVPDA/C ₆₀ (89 : 10 : 1)	8.9	0.09
BEOPEA/NVPDA/C ₆₀ (64 : 35 : 1)	13	0.15

*Each composite was crosslinked at 130°C for 45 min and applied electric field was 70 V/ μ m.

which was crosslinked at 80°C for 30 min (condition A) and at 100°C for 45 min (condition B), respectively. The differences of figure type indicate that orientational effect plays main role in condition A but permanent poling effect in condition B. Most chromophores could be oriented after poling because the acetylene moiety is not completely crosslinked in condition A. The field dependence of the optical gain at condition A shows E³ dependence indicating orientation enhancement. However, the device prepared at condition B shows quadratic field dependence of the optical gain which is coincidence with theoretical results. At 70 V/ μ m the coupling gain of 13 cm⁻¹ was obtained for the BEOPEA/NVPDA/C₆₀ composite (64:35:1). The value is very high in the permanent poled photorefractive device and the device shows the availability of practical application.

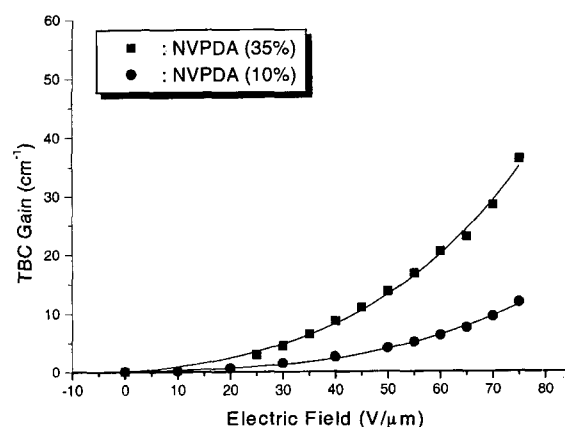


Figure 4. Electric field dependence of the two beams coupling gain at 10% and 35% chromophore concentrations; crosslinking condition is 80 and 30 min (condition A).

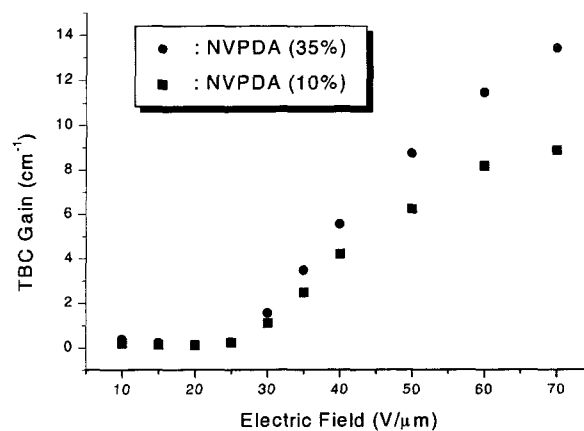


Figure 5. Electric field dependence of the two beams coupling gain at 10% and 35% chromophore concentrations; crosslinking condition is 100°C, 45 min (condition B).

CONCLUSIONS

The photorefractive composite was prepared from newly synthesized crosslinkable matrix (BEOPEA) which have hole transporting property. 2BC and FWM studies show photorefractivity. Thermal crosslinking of the matrix after poling is stable and lasts at least for a few days. Many problems such as intrinsic instability, phase separation, difficulty in rational design and thick film preparation that are faced in many composite materials or multifunctional high T_g polymers can be overcome in this composite system.

Acknowledgements - This work was supported by R05-2002-000-01419-0 from the Basic Research Program of the Korea Science & Engineering Foundation (KOSEF).

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[#]This publication is dedicated to the memory of the late Professor Sang Chul Shim (KAIST), deceased on April 10, 2002.

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