

# Synthesis and characterization of photoconducting non-linear optical polymers containing indole-benzoxazole moiety

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Received 3 April 2000; received in revised form 29 August 2000; accepted 1 September 2000

## Abstract

2-[3-(6-Nitro-benzoxazol-2-yl)-indol-1-yl]-ethanol (**5**) was synthesized as a photoconducting non-linear optical (NLO) chromophore with thermal and photochemical stabilities and broad transparency at the visible region. The peak wavelength of optical absorption was ca. 100 nm blue-shifted compared to those of conventional NLO chromophores, DANS or DR1. Methacrylate and acrylate ester of **5** were synthesized and subsequently copolymerized with methyl methacrylate and methyl acrylate, respectively, to give photoconducting NLO polymers. To further enhance the photoconductive sensitivity, hydrazone-containing methacrylate monomer was also copolymerized with **5**. Alternatively photoconducting plasticizer *N'*-[9-(2-ethyl-hexyl)-9*H*-carbazol-3-ylmethylene]-*N,N*-diphenyl-hydrazone (EHCzHy) was mixed with simple copolymer (PIDBAC13) to give polymer composites with enhanced photoconductivity and reduced glass transition temperature ( $T_g$ ). Photorefractivity was demonstrated for the 70:30 composite of PIDBAC13/EHCzHy doped with 0.2% thiapyrilium salt ( $T_g \sim 61^\circ\text{C}$ ) through the two-beam coupling and four-wave mixing. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Indole; Benzoxazole; Photorefractive polymer

## 1. Introduction

Photorefractive polymers have attracted considerable attention owing to their potential applications including high-density optical data storage, optical image processing, phase conjugation, lasing, dynamic holography, optical computing and pattern recognition [1]. The necessary characteristics for a material to be regarded as potentially photorefractive are photoconductivity and electro-optic (EO) property. Therefore, a candidate photorefractive polymer can be made by either incorporating these properties directly into polymer (fully functionalized polymer) [2–5] or doping guest molecules into the polymer (guest–host polymer composite) [6–9] to produce these properties.

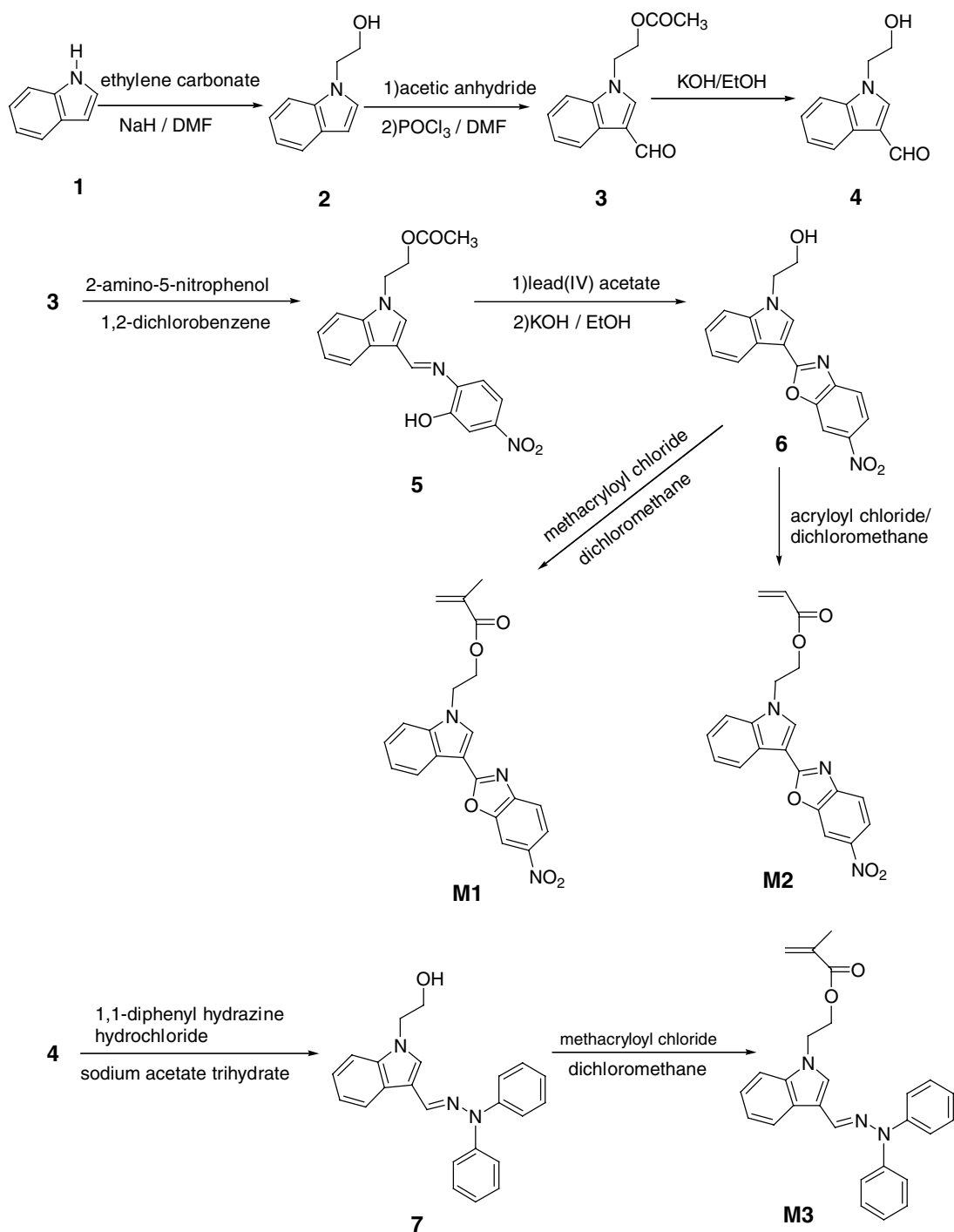
Most of the photorefractive polymers reported to date are based on the guest–host polymer composite, which normally consists of four components (photoconducting polymer host, NLO chromophore, plasticizer and photosensitizer). Although it is facile and versatile to prepare a guest–host polymer composite, there are inherent problems, such as phase separation, which limits the concentration of dopants, and also the trade-off of photoconductivity and EO property with composi-

tion. To enhance EO property, for example, it is necessary to increase the concentration of the NLO chromophore, which adversely leads to the phase separation and decrease of photoconductivity. In this context, the photoconducting NLO chromophore, which possesses both functionalities in a single molecule, is the right answer to this trade-off problem. The use of photoconducting NLO chromophore suppresses phase separation, and simultaneously increases EO property and photoconductivity.

We have synthesized and reported various photoconducting NLO chromophores based on the heteroaromatic donor moiety like carbazole [10], indole [11] and indoline [12] linked with stilbene as  $\pi$ -conjugation bridge and nitro group as electron acceptor. It was shown that polymethacrylates containing these chromophores as a side chain exhibited excellent EO property and moderate photoconductivity. Three practical problems, however, were realized when we tried to utilize these polymers as photorefractive media. First, the absorption maxima ( $\lambda_{\text{max}}$ s) of these chromophores were located at wavelengths longer than 420 nm with their apparent cut-off usually extended to 600 nm and more. Such an insufficient transparency in the visible region is a real problem, since even a small tailing absorption at the wavelength of the laser source (for example, 532 or 633 nm) is large enough to prevent

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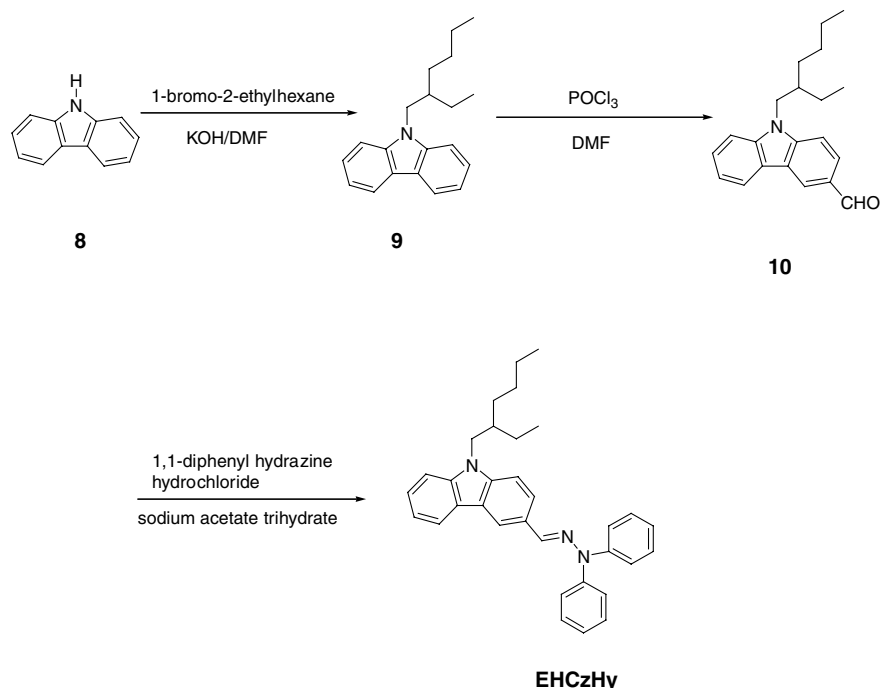


Scheme 1.

the polymer from getting photorefractive net gain. Secondly, the  $T_g$ s of polymethacrylates were too high to be poled at room temperature. Thirdly, the photoconductive sensitivity of photoconducting NLO chromophore was not high enough to ensure a fast response.

In order to address these problems, we designed and synthesized novel photoconducting NLO chromophore, 2-[3-(6-nitro-benzoxazol-2-yl)-indol-1-yl]-ethanol in this work. The EO property is attributed to the conjugated

push-pull structure of this chromophore. Indole, the hetero-aromatic structure like carbazole, was designed to work as photoconducting moiety as well as electron donor. Indole was adopted over carbazole for this purpose, because indole provides better poling efficiency owing to the more compact size compared with carbazole [11]. Benzoxazole moiety was introduced as  $\pi$ -conjugated bridge instead of the conventional stilbene unit to obtain blue-shifted absorption together with the enhanced thermal and photochemical



Scheme 2.

stability. Finally, to increase the photoconductive sensitivity for fast response, we also designed and synthesized photoconducting chromophore, 2-[3-(diphenyl-hydrazonomethyl)-indol-1-yl]-ethanol and photoconducting plasticizer, *N'*-[9-(2-ethyl-hexyl)-9*H*-carbazol-3-ylmethylene]-*N,N*-diphenyl-hydrazine (EHCzHy). The former was introduced to polymethacrylate through copolymerization with photoconducting NLO monomer, and the latter was molecularly doped to polyacrylates which yielded polymer composites of low  $T_g$ . Meerholz et al. [13] reported that a net gain of  $200 \text{ cm}^{-1}$  was obtained by using photoconducting plasticizer, *N*-ethylcarbazole (ECZ), but crystallization of ECZ led to the critical problem of durability since it was a crystalline solid [14]. To overcome this problem, flexible ethyl hexyl group was introduced to our plasticizer, which resulted in glassy material having  $T_g$  below room temperature. ( $T_g = 22^\circ\text{C}$ ). The Polymer composite of simple copolymer PIDBAc13 and EHCzHy in 70:30 ratio was perfectly miscible to yield a stable amorphous film. We report the details of the photoconductivity and EO properties of all polymer samples synthesized in this work. Preliminary results of photorefractivity measurement with PIDBAc13/EHCzHy are also included only as a demonstration of potential applicability.

## 2. Experimental

### 2.1. Instrumental analyses

$^1\text{H}$  NMR spectra were recorded with the use of Jeol

JNM-LA300 spectrometer. IR spectra were measured with KBr pellet or KBr windows on a Midac FT-IR spectrophotometer. Mass spectrometer data were obtained from JMS AX505WA using electron impact (EI) mode. Shimadzu UV 2101PC double beam spectrophotometer was used for the UV–visible absorption spectra. Gel permeation chromatography (GPC) was performed at the flow rate of 1.0 ml/min in THF at  $30^\circ\text{C}$  with Waters HPLC component system equipped with five Ultra- $\mu$ -styragel<sup>®</sup> columns ( $2 \times 10^5$ ,  $10^5$ ,  $10^4$ ,  $10^3$ ,  $500 \text{ \AA}$ ), which was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out under nitrogen atmosphere at the heating rate of  $20^\circ\text{C}/\text{min}$  on Perkin Elmer DSC7 and  $10^\circ\text{C}/\text{min}$  on Du Pont 2950, respectively.

### 2.2. Synthesis of monomers

Synthetic pathway to the photoconducting NLO monomers, 2-methyl-acrylic acid 2-[3-(6-nitro-benzoxazol-2-yl)-indol-1-yl]-ethyl ester (M1), and acrylic acid 2-[3-(6-nitro-benzoxazol-2-yl)-indol-1-yl]-ethyl ester (M2), the comonomer for enhanced carrier mobility, 2-methyl-acrylic acid 2-[3-(diphenyl-hydrazonomethyl)indol-1-yl]-ethyl ester (M3), and functional plasticizer, *N'*-[9-(2-ethyl-hexyl)-9*H*-carbazol-3-ylmethylene]-*N,N*-diphenyl-hydrazine (EHCzHy) is outlined in Schemes 1 and 2, which show the synthesis of monomers and the synthesis of the plasticizer, respectively.

Synthesis of aldehyde derivatives **3** and **4** was reported earlier by us [11]. The synthesis of the photoconducting

Table 1  
Copolymerization conditions

Copolymer	Monomer (g)	Comonomer (g)	Feed mole ratio	AIBN (initiator)	NMP (ml)	Yield (%)
PIDBM11	M1 (0.4)	Methyl methacrylate (0.10)	1:1	16.7 mg (5 mol%)	4	80
PIDBM13	M1 (1)	Methyl methacrylate (0.77)	1:3	12.6 mg (0.75 mol%)	11	71
PIDBM19	M1 (0.8)	Methyl methacrylate (1.84)	1:9	25 mg (0.75 mol%)	10	72
PIDBHy11	M1 (0.55)	M3 (0.6)	1:1	23.3 mol (5 mol%)	11	87
PIDBAc13	M2 (1.0)	Methyl acrylate (0.68)	1:3	87 mol (5 mol%)	10	53

plasticizer outlined in Scheme 2 was also reported earlier by us [11]. Benzoxazole formation from **3** was carried out by two-step synthesis adapting the methods reported in Ref. [15].

*Acetic acid 2-[3-(2-hydroxy-4-nitrophenylimine-methyl)-indol-1-yl]-ethyl ester (5)*. To a boiling solution of 1.1 g (4.7 mmol) of **3** in 15 ml of 1,2-dichlorobenzene, 0.87 g (5.6 mmol) of 2-amino-5-nitrophenol was added under magnetic stirring. The reaction mixture was boiled for 2 h. After cooling the solution was poured into cold *n*-hexane, and the precipitate was filtered. The solid was dissolved in dichloromethane, precipitated with *n*-hexane twice, and dried to yield 1.37 g (79%) of orange solid. According to the  $^1\text{H}$  NMR spectrum, the crude product was considered to be pure enough for use in the subsequent cyclization step.

*2-[3-(6-Nitro-benzoxazol-2-yl)-indol-1-yl]-ethanol (6)*. 1 g (2.7 mmol) of **5** was dissolved in 20 ml of dichloromethane. Under magnetic stirring, 1.2 g (2.7 mmol) of lead(IV) acetate was added in portions. The mixture was stirred at room temperature for 1 h to give a solution with a small amount of suspended solids. After filtration, the solution was washed with water and the solvent was removed at reduced pressure. This crude product was used in the successive hydrolysis step. It was dissolved in 50 ml of ethanol, and 0.3 g (5.4 mmol) of KOH was added. The solution was mildly heated under magnetic stirring for 1 h, and neutralized by HCl. After cooling, the precipitate was filtered and recrystallized from ethanol to yield 0.8 g of yellow solid (91%); mp 231°C;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  8.63 (d, 1H;  $J = 2.19$ ), 8.47 (s, 1H), 8.34 (m, 1H), 8.28 (q, 1H;  $J = 2.19, 8.82$ ), 7.89 (d, 1H;  $J = 8.82$ ), 7.71 (m, 1H), 7.35 (m, 2H), 5.03 (t, 1H), 4.40 (t, 1H), 3.79 (q, 1H); IR (KBr pellet,  $\text{cm}^{-1}$ ) 3530 ( $\nu_{\text{O-H}}$ ), 1577 and 1326 ( $\nu_{\text{nitro}}$ );  $m/z$  (EI, low resolution) calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_4$ , 323.40, found 323.

*2-[3-(Diphenyl-hydrazonomethyl)-indol-1-yl]-ethanol (7)*. To a magnetically stirred solution of 1.4 g (6.36 mmol) of 1,1-diphenylhydrazine hydrochloride in 40 ml of ethanol was added 1.29 g (9.54 mmol) of sodium acetate trihydrate at room temperature. Then a solution of **4** (1 g, 5.3 mmol) in 40 ml ethanol was added dropwise for 30 min. After stirring for 3 h, ethanol was removed under reduced pressure and the residue was poured into water. The product was extracted with chloroform, washed with plenty of brine and distilled water, and dried over  $\text{MgSO}_4$ . The solvent, chloroform was removed under reduced pressure. The crude product was

purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1:1) to yield 1.45 g of white solid (94%); mp 145°C;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  8.33 (t, 1H), 7.54–7.42 (m, 7H), 7.24–7.14 (m, 8H), 4.87 (t, 1H), 4.15 (t, 1H), 3.67 (q, 1H); IR (KBr pellet,  $\text{cm}^{-1}$ ) 3412 ( $\nu_{\text{O-H}}$ ) 1597 ( $\nu_{\text{C=N}}$ );  $m/z$  (EI, low resolution) calcd for  $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_1$ , 355.43, found 355.

*2-Methyl-acrylic acid 2-[3-(6-nitro-benzoxazol-2-yl)-indol-1-yl]-ethyl ester (M1)*. To a magnetically stirred solution of 3 g (9.28 mmol) of **6** and 2.82 g (27.83 mmol) of triethylamine in 50 ml of dichloromethane, 1.94 g (18.56 mmol) of methacryloyl was added dropwise at 0°C. After stirring for 1 h, the resulting solution was allowed to warm up to room temperature. After another 1 h the solution was washed with brine and water, dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. The yellow residue was purified by silica gel column chromatography (ethyl acetate/dichloromethane = 1:15) and recrystallization from ethyl acetate to yield 2.1 g of yellow solid (60%); mp 195.8°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.47 (m, 1H), 8.45 (d, 1H), 8.31 (q, 1H), 8.13 (s, 1H), 7.78 (d, 1H), 7.50 (m, 1H), 7.41 (m, 2H), 6.06 (s, 1H), 5.58 (s, 1H), 4.57 (s, 4H), 1.89 (s, 3H); IR (KBr pellet,  $\text{cm}^{-1}$ ); 1700 ( $\nu_{\text{C=O of ester}}$ ), 1589 and 1330 ( $\nu_{\text{nitro}}$ );  $m/z$  (EI, low resolution) calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_5$ , 391.38, found 391.

*Acrylic acid 2-[3-(6-nitro-benzoxazol-2-yl)-indol-1-yl]-ethyl ester (M2)*. M2 was synthesized and purified similarly from 0.5 g (1.55 mmol) of **6**, 0.47 g (4.64 mmol) of triethylamine in 30 ml of dichloromethane and 0.28 g (3.09 mmol) of acryloyl chloride (0.34 g, 58%); mp 179°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.45 (m, 1H), 8.43 (d, 1H), 8.30 (q, 1H), 8.13 (s, 1H), 7.76 (d, 1H), 7.48 (m, 1H), 7.40 (m, 2H), 6.37 (q, 1H), 6.23 (q, 1H), 5.84 (q, 1H), 4.57 (s, 4H); IR (KBr pellet,  $\text{cm}^{-1}$ ) 1724 ( $\nu_{\text{C=O of ester}}$ ), 1596 and 1334 ( $\nu_{\text{nitro}}$ );  $m/z$  (EI, low resolution) calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_5$ , 377.35, found 377.

*2-Methyl-acrylic acid 2-[3-(diphenyl-hydrazonomethyl)-indol-1-yl]-ethyl ester (M3)*. This monomer was prepared from **7** (2.00 g, 5.82 mmol), triethylamine (1.8 g, 17.46 mmol), and methacryloyl chloride (1.2 g, 11.64 mmol) in 30 ml of dichloromethane by the same procedure as described for M1 (1.6 g, 66%); mp 108°C;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  8.31 (m, 1H), 7.59–7.40 (m, 7H), 7.25–7.13 (m, 8H), 5.84 (s, 1H), 5.57 (s, 1H), 4.45 (t, 2H), 4.36 (t, 2H), 1.71 (s, 3H); IR (KBr pellet,  $\text{cm}^{-1}$ ) 1722 ( $\nu_{\text{C=O of ester}}$ ), 1580 ( $\nu_{\text{C=N}}$ );  $m/z$  (EI, low resolution) calcd for  $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_2$ , 423.51, found 423.

Table 2  
Physical properties of copolymers

Copolymer	$m_{\text{pol}}^a$	$M_w^b$	$M_w/M_n$	$T_g$ (°C)	$\lambda_{\text{max}}$	$\lambda_{\text{cut-off}}$
PIDBM11	1:0.9	49 000	4.9	149	— <sup>c</sup>	— <sup>c</sup>
PIDBM13	1:1.3	57 100	2.7	149	380	487
PIDBM19	1:5.6	200 000	6.5	143	— <sup>c</sup>	— <sup>c</sup>
PIDBHy11	—	22 000	2.0	145	358	520
PIDBAc13	1:1.1	7500	1.7	96	— <sup>c</sup>	— <sup>c</sup>

<sup>a</sup> Mole ratio in the copolymer, determined by elemental analysis.

<sup>b</sup> Measured by GPC in THF.

<sup>c</sup> Considered to be the same as PIDBM13.

### 2.3. Polymerization

Photoconducting NLO polymers, PIDBM1X and PIDBHy11, were obtained by free radical copolymerization of M1 with methyl methacrylate (MMA) in different feed mole ratio (1:1, 1:3, 1:9), and with M2 in feed mole ratio 1:1, respectively. 2,2-Azobisisobutyronitrile (AIBN) was used as radical initiator and *N*-methyl pyrrolidinone (NMP) as solvent. Polyacrylate, PIDBAc13 was prepared by the same method. Polymerization conditions and polymer code are summarized in Table 1. Typical polymerization procedure is described below.

0.4 g (1.02 mmol) of M1, 0.102 g (1.02 mmol) of MMA and 0.0167 g (0.102 mmol) of AIBN were dissolved in 5 ml of NMP. The solution was degassed by standard vacuum-freeze–thaw technique. After sealing the degassed ampoule, the reaction mixture was heated at 65°C for 48 h. After cooling, the resulting solution was diluted to twice its original volume with tetrahydrofuran (THF) and poured into methanol to precipitate the polymer PIDBM11, which was purified by repeated reprecipitation from chloroform to methanol till monomers were not detected by thin layer chromatography (0.4 g, 80%).

### 2.4. Preparation of polymer film

Polymers were dissolved in THF (10 wt%) and the solution was filtered with a Teflon membrane filter (Millipore, 0.22 μm). Thin polymer films of ~1 μm thickness were spin-coated at 1500 rpm on to indium–tin-oxide (ITO) coated glass. Residual solvent was removed by heating the films in vacuum oven for several days. Film thickness was measured with TENCOR P-10 profilometer.

Polymer composite, PIDBAc13/EHCzHy was prepared in different composition ratio for measurements of photorefractivity. A small amount (0.2 wt%) thiapyrillium salt (TPY-salt) was added to affect the photocarrier generation at 633 nm [16]. The sample was dissolved in dichloroethane and filtered through a Teflon membrane filter. The solution was cast over a Teflon plate and dried in vacuum above  $T_g$ , till the solvent was removed completely. The obtained thick polymer film was sandwiched between ITO glasses or slide

glasses. Thickness was controlled to be 125 μm by using polyimide film as a spacer.

### 2.5. EO properties

For the measurement of the EO coefficient ( $r_{33}$ ), contact poling was carried out. A gold electrode was sputter-coated in  $10^{-6}$  Torr vacuum on the polymer film backed with ITO glass. To align the chromophores, the sample was heated and then the appropriate poling voltage was applied to the gold electrode. After 15 min, the film was cooled down to room temperature, and the poling voltage was removed. The electro-optic coefficients of the poled polymers were measured at the wavelength of 633 nm (He–Ne laser) using a simple reflection method [17].

### 2.6. Photoconductivity

The dark and the photoconductivities of the polymer films were evaluated by measuring a current through the polymer film sandwiched between gold and ITO using the Keithley 617 electrometer, and He–Ne laser was used as a light source. A positive voltage was applied to the ITO electrode and the light was shed through the ITO electrode. Photoconductive sensitivity was calculated as the ratio of photoconductivity to the light intensity.

### 2.7. Photorefractivity

Photorefractivity was studied by two-beam coupling and four-wave mixing at the electric field of 30 V/μm. In both experiments, the normal of the sample surface was tilted 60° with respect to the symmetric axis of the two intersected beams, and the external inter-beam angle was 11°. For two-beam coupling, the grating translation technique was used to deduce the phase shift of the space-charge field [18,19].

## 3. Results and discussion

### 3.1. Synthesis of monomers and plasticizer

Photoconducting NLO chromophore with benzoxazole moiety was synthesized through the three-step reactions of indole aldehyde derivative **3** and 2-amino-5-nitrophenol, i.e. formation of Schiff base, oxidative ring closing and deprotection. Because the hydroxy group normally reduces the solubility of Schiff base and leads to various side reactions, deprotection was carried out after ring closing. Photoconducting indole-hydrazone chromophore **7** was prepared from **4** and 1,1-diphenyl hydrazine hydrochloride. In this case, deprotection in alkaline condition was carried out before the formation of hydrazone, since the azomethine bond in hydrazone is unstable in alkaline condition. The reaction of these chromophores with methacryloyl chloride and acryloyl chloride yielded photoconducting NLO monomers (M1, M2) and photoconducting comonomer (M3),

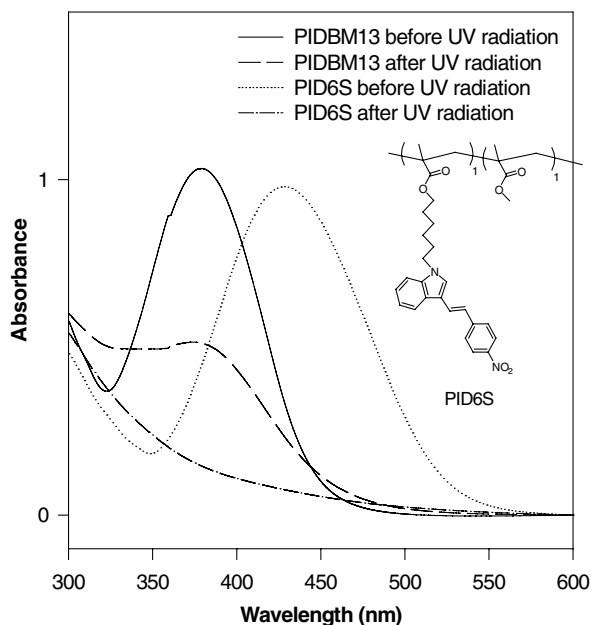


Fig. 1. UV-visible spectra of PIDBM13 and PID6S films before and after UV irradiation.

respectively. Photoconducting plasticizer (EHCzHy) was similarly synthesized as reported earlier [11].

### 3.2. Physical properties of polymers

Photoconducting NLO polymers were prepared by free radical polymerization. All the polymers were very soluble in organic solvents like chloroform, dichloromethane and dichloroethane. Their molecular weights, glass transition temperatures and optical properties are summarized in Table 2. Owing to the good solubilities and moderate to high molecular weights, thin polymer films of high optical and mechanical quality could be easily fabricated by spin coating. The wavelength of maximum absorption of the

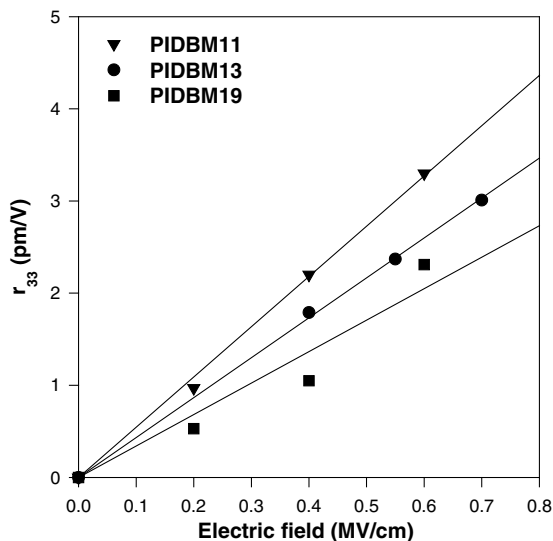


Fig. 2. Electro-optic coefficients of PIDBM1X.

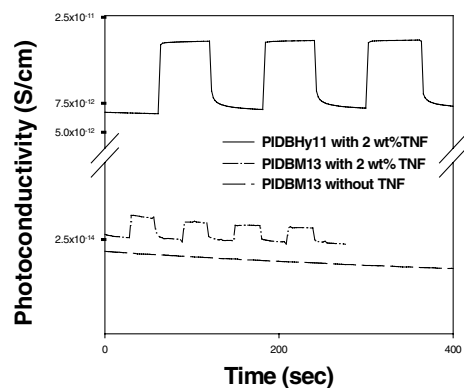


Fig. 3. Photocurrent response of PIDBM13 and PIDBHy11, as laser was on/off.

indole-benzoxazole polymer (represented by PIDBM13) is 380 nm, though that of indole-stilbene (PID6S, see the inset of Fig. 1 for the structure) reported earlier [11] was 422 nm, which resulted in excellent transparency and reduced the absorption coefficient over a long range, especially at 633 nm. Compared to the conventional DANS or DR1 polymer, more than 100 nm blue-shift was achieved with the indole-benzoxazole polymer. To confirm thermal and photochemical stabilities of polymers containing the indole-benzoxazole moiety, they were also compared with those of indole-stilbene polymer (PID6S). TGA thermograms showed that PIDBM11 was stable up to 326°C (temperature of 2% weight loss, under nitrogen), which is higher than PID6S by 50°C. To investigate the photochemical stability against UV light, both the films of PIDBM13 and PID6S were exposed to UV light (400-W Hg-Xe lamp) for 1 h, and decreases of absorbance were observed (Fig. 1). Though absorption of PIDBM13 is higher than PID6S at the UV region, the absorbance of PIDBM13 was less decreased than that of PID6S after exposure to UV light. This result demonstrates that the indole-benzoxazole polymer is much more stable than the indole-stilbene polymer.

### 3.3. EO property and photoconductivity

The EO property requires that the total system does not possess a center of symmetry. In polymers, this can be achieved by the poling process at temperatures around  $T_g$ . Generally, the degree of poling is monitored by UV-visible spectroscopy, and expressed as an order parameter,

$$\Phi = 1 - (A_p/A_0)$$

where  $A_p$  is the absorbance of the poled film and  $A_0$  is that of the unpoled one. The order parameter of PIDBM13 was 0.22 after it was poled at 5 kV and 150°C, which was twice that of the polymer containing carbazole [20]. This result suggests that polymers containing indole possess better poling efficiency than polymers containing carbazole, which justifies our molecular design of indole-based

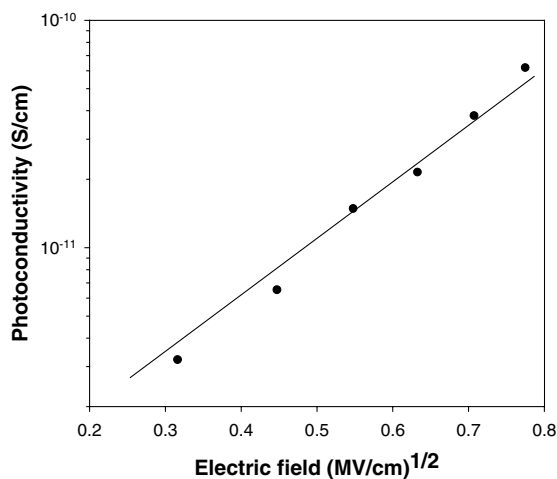


Fig. 4. Electric field dependence of photoconductivity of PIDBHy11.

chromophore. The measurement results of EO properties are plotted in Fig. 2. EO coefficients increased in proportion to the poling field and concentration of chromophores. The  $r_{33}$  of PIDBM11 was 3.3 pm/V at the poling electric field of 0.6 MV/cm. Although the value is small, it is a non-resonant one and further increase will be obtained at a higher poling electric field.

For the measurement of photoconductivity, we used only a He–Ne laser with intensity of 98 mW/cm<sup>2</sup> with which photorefractive measurements were performed. As shown in Fig. 3, PIDBM13 without 2,4,7-trinitro-9-fluorenone (TNF) has no photoconductive response since it has no absorption at 633 nm. However, TNF-sensitized PIDBM13 (2 wt%) shows a distinct photoconductive response, which results from the formation of a charge transfer (CT) complex. Its photoconductive sensitivity was  $2.6 \times 10^{-13}$  S cm<sup>-1</sup>/W cm<sup>-2</sup> under the electric field of 0.4 MV/cm. As shown in Fig. 3, the hydrazone-containing

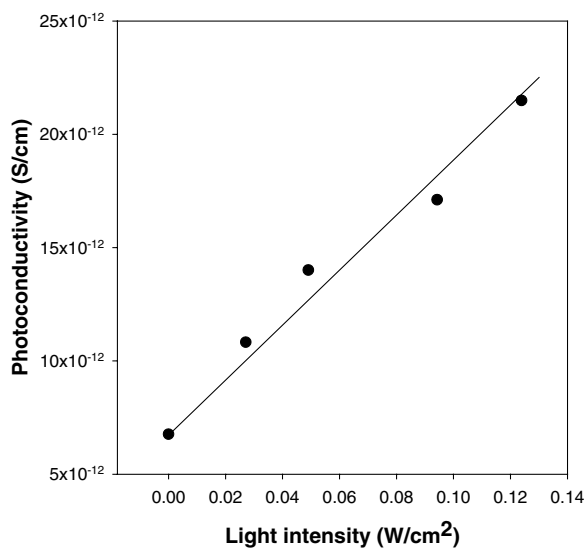


Fig. 5. Light dependence of photoconductivity of PIDBHy11.

copolymer has orders of magnitude larger photoconductive sensitivity than that of PIDBM13. These results suggest that PIDBHy11 possesses a more efficient charge transporting property than PIDBM13, which is, no doubt, because M3 contains the indole-hydrazone moiety with enhanced carrier transporting property. In Figs. 4 and 5, electric field and light intensity dependence of TNF-sensitized PIDBHy11 are shown. As expected, the photoconductivity was directly proportional to the laser intensity and it increased as the applied electric field increased. The photoconductive sensitivities were  $1.7 \times 10^{-10}$  S cm<sup>-1</sup>/W cm<sup>-2</sup> and  $5.0 \times 10^{-10}$  S cm<sup>-1</sup>/W cm<sup>-2</sup> under 0.4 and 0.6 MV/cm, respectively.

### 3.4. Photorefractivity of polymer composite

Polymer composites for the preliminary and demonstrative photorefractivity measurements were prepared from polyacrylate PIDBAc13 and functional plasticizer EHCzHy to get a low- $T_g$  polymer system, because the high- $T_g$  system is very difficult and sophisticated for the sample preparation and characterization of photorefractivity. We are currently challenging the photorefractivity measurement of the high- $T_g$  polymer system and it will be the subject of our next paper. To investigate the miscibility and  $T_g$  of the polymer composite by DSC, we prepared four polymer composites in ratios of 80:20, 70:30, 60:40 and 50:50 of PIDBAc13/EHCzHy. While 80:20 and 70:30 composites exhibited only a single  $T_g$ , and proved their compatibility, 60:40 and 50:50 composite showed two different  $T_g$ s, which were those of polymer and plasticizer. While the  $T_g$  of the photoconducting NLO polymer (PIDBAc13) was 96°C, those of the 70:30 and 80:20 composites were 61 and 73°C, respectively.  $T_g$  of the 70:30 composite was lower than that of the 80:20 composite by 12°C, owing to a greater content of plasticizer, so we chose the 70:30 composite for the photorefractive measurements and 0.2 wt% of TPY-salt as photosensitizer was added to give the photorefractive polymer composite P1. The linear absorption spectra of the 70:30 composites and P1 are shown in Fig. 6.  $\lambda_{\max}$  and  $\lambda_{\text{cut-off}}$  of the 70:30 composite without photosensitizer were 352 and 463 nm, respectively. The addition of photosensitizer slightly increased the absorption in the red and near-infrared region, which is certainly a result of the absorption by this salt. The absorption coefficient of P1 at 633 nm, where the photorefractive measurements were performed, was 11.3 cm<sup>-1</sup> as shown in the inset of Fig. 6. No evidence of crystallization and phase separation was observed in the polymer composite even after several months. As the first step of the photorefractivity measurement, we tried to identify two-beam coupling gain and diffraction efficiency of P1 only at room temperature without performing any electric-field poling at higher temperature. Since the  $T_g$  of P1 is 61°C, we did not expect to get large values at room temperature; instead, we hoped to demonstrate the photorefractivity to justify our molecular design and synthesis.

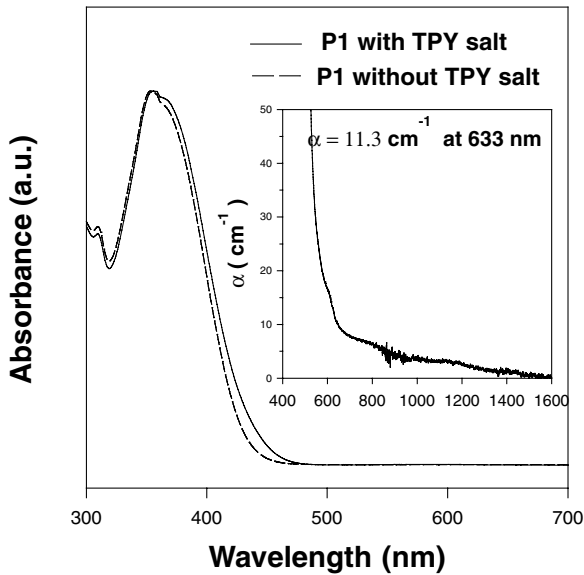


Fig. 6. UV-visible spectra of P1 with and without TPY-salt. The inset shows absorption coefficient at 633 nm.

The photorefractivity was studied by two-beam coupling and four-wave mixing at the electric field of 0.3 MV/cm. In both experiments, the normal of the sample surface was tilted  $60^\circ$  with respect to the symmetric axis of the two intersected beams, and the external inter-beam angle was  $11^\circ$ . For two-beam coupling, the grating translation technique was used to deduce the phase shift of the space-charge field. While the sample was translated by  $14.3 \mu\text{m}$  for 0.3 s, asymmetric energy transfer between two p-polarized beams, which is a unique and definite proof of photorefractivity, was clearly measured (Fig. 7). The gain coefficient was  $1.4 \text{ cm}^{-1}$  and the phase shift was  $56^\circ$  for P1. In four-wave mixing, two s-polarized beams were used as writing beams, and a p-polarized beam as probe beam. As shown in Fig. 8, 0.018% of diffraction efficiency was obtained. Much higher values of gain coefficient and diffraction efficiency are

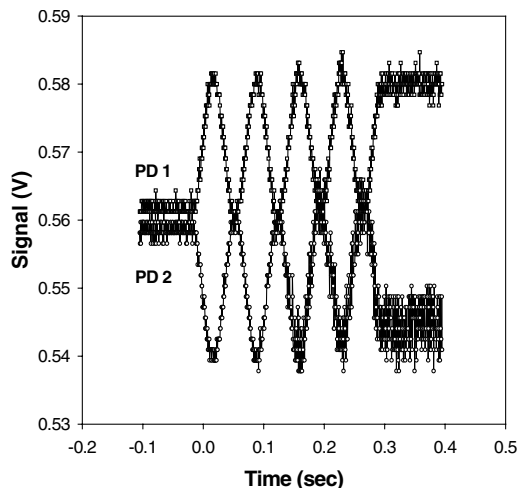


Fig. 7. Asymmetric energy transfer in P1.

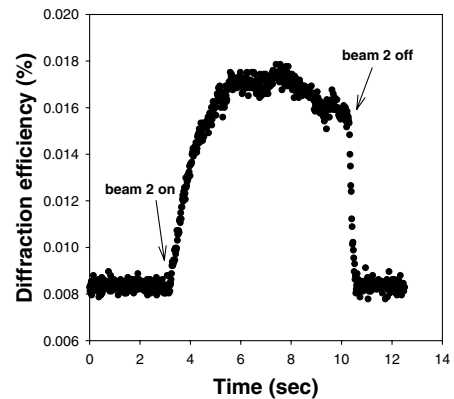


Fig. 8. Diffraction efficiency of P1, as beam 2 was switched on/off.

expected by poling the polymer composite at around  $T_g$  or alternatively by properly adjusting the composition of this composite to lower the  $T_g$  down to ambient temperature.

#### 4. Conclusions

We synthesized the novel photoconducting NLO polymer containing indole-benzoxazole moiety as  $\pi$ -conjugation bridge with excellent thermal and photochemical stability. The optical absorption of the indole-benzoxazole polymer was  $\sim 100 \text{ nm}$  blue-shifted compared to those of conventional NLO polymers, providing a broad transparent window in the visible region. Preliminary measurements of photorefractivity showed that our polymers are potential candidates for the photorefractive application.

#### Acknowledgements

This work was supported by the Korea Ministry of Education Research Fund for Advanced Materials (RIAMI-NE22-97). Supplementary experiments after this contract period were partly supported by CRM-KOSEF.

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