Synthesis and Properties of Photorefractive Polymers Containing Indole-Based Multifunctional Chromophore as a Pendant Group

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ABSTRACT: Novel photorefractive chromophores with indole and nitrobenzene as the push and pull groups, respectively, were synthesized and subsequently reacted with methacryloyl and acryloyl chloride to give multifunctional monomers. Polymers were obtained by copolymerization of these monomers with methyl methacrylate (**P1**, **P2**) or butyl acrylate (**P3**). These polymers were very soluble in organic solvents to be fabricated into optically clear polymer films and showed glass transition (T_g) at ca. 150 °C for **P1**, **P2** and at 8 °C for **P3**, respectively. Large nonlinear optical coefficients (d_{33} as high as 49 pm/V) and photoconductive sensitivity (on the order of 10^{-9} S·cm^{-1}/W·cm^{-2}) were identified with high T_g polymers **P1** and **P2**. Preliminary investigation of photorefractivity was carried out with low T_g polymer (**P3**) by two-beam coupling and four-wave mixing experiments. It was observed that **P3** doped with 1% TNF showed two-beam coupling gain of 2.2 cm^{-1} at 75 V/μm and diffraction efficiency of 0.44% at 60 V/μm. When the photoconducting plasticizer (**EHCzHy**) was added to **P3**, a net gain of 22 cm^{-1} and a diffraction efficiency of 2.41% could be achieved.

Introduction

Photorefractive materials are potentially useful for the high-density optical data storage, image processing, dynamic holography, and optical computing. Among various class of materials, photorefractive polymers are the most promising since they possess outstanding and unique advantages such as the highest figure of merit, compositional flexibility, unlimited molecular design, ease of fabrication, low dielectric constant, and low cost over the inorganic ferroelectric crystals exhibiting photorefractivity.[1,2] It is well-known that photorefraction is revealed as the combined activity of nonlinear optical (NLO) effect and photoconductivity. Therefore, photorefractive polymers are normally multicomponent system which comprises both NLO and photoconducting chromophore as the guest[3−6] or pendant group.[7−10]

The use of individual chromophores for optical nonlinearity and photoconductivity, however, is usually accompanied by the phase segregation, difficulties in the synthesis, and compositional control for the optimized photorefractivity.

As a different approach to avoid these problems, multifunctional photorefractive chromophores which exhibit both the photoconductivity and NLO activity have been recently reported by many investigators.[11−13] Carbazole-based push−pull type NLO molecules are typical examples of multifunctional photorefractive chromophore. Photoconducting NLO properties of polymers containing side-chain carbazole-based multifunctional chromophore have been reported earlier by us,[14−16] and the photorefractivity of the main chain polymer was also demonstrated by Zhang et al.[17] Serious problems with carbazole-containing chromophores, however, were encountered during poling. It was noted that the higher degree of dipolar ordering and consequently the higher value of NLO coefficients could not be achieved for these photoconducting NLO polymers, presumably due to the limited orientational mobility of the very bulky carbazole-containing chromophore. Reported values of the second-harmonic generation (SHG) coefficient, d_{33}, are mostly less than 22 pm/V.[14,17−19]

To improve the poling behavior and consequent photorefractive performance, we came to consider the use of the indole moiety as a substitute for carbazole in the design of the photorefractive chromophore. This adoption of indole as the push group of photoconducting NLO chromophore is based on the consideration that it is smaller than carbazole but is likely to keep photoconductivity to some extent due to its fused heteroaromatic structure similar to carbazole.

In this work, we report the synthesis and properties of indole-based photoconducting NLO chromophores and polymers. We demonstrate the photorefractive performance of these multifunctional polymers and also the methods that enhance their photorefractivity by use of a photoconducting plasticizer.

Experimental Section

Instruments. ^{1}H NMR spectra were recorded with the use of a Varian 200 spectrometer or a Bruker AM-300 spectrometer. IR spectra were measured with KBr pellet or KBr windows on a Midac FT-IR spectrophotometer. A JASCO V-530 spectrometer was used for UV−vis absorption spectra. Gel permeation chromatography (GPC) was carried out at a flow rate of 1.0 mL/min in THF at 30 °C with Waters HPLC component system equipped with five Ultra-μ-styragel columns (2×10^5, 10^5, 10^4, 10^3, 500 Å), which were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed under nitrogen atmosphere on a Perkin-Elmer DSC7 at a heating rate of 10 °C/min.

Materials. Methacryloyl chloride (Acros Organics, 97%), acryloyl chloride (Acros Organics, 98%), methyl methacrylate (Aldrich Chemical Co., 99%), butyl acrylate (Aldrich Chemical Co., 99+%) and *N*-methylpyrrolidinone (Aldrich Chemical Co., 99.5%) were fractionally distilled. The initiator, 2,2'-azobis-

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(isobutyronitrile) (Aldrich Chemical Co., 98%), was recrystallized from methanol. All other reagents and starting materials were purchased from Aldrich Chemical Co. and used as received unless otherwise noted.

Synthesis of Chromophores and Monomers. 2-(1*H*-1-Indolyl)-1-ethanol (1). A solution of 21.2 g (182 mmol) of indole in 600 mL of dry dimethylformamide (DMF) was vigorously stirred at 0 °C and treated with 10.8 g (1.00 equiv) of sodium hydride (60% oil dispersion). After the mixture was stirred for 3 h, 9.04 g (210 mmol) of ethylene carbonate was slowly added. The mixture was stirred at 0 °C for 1 h and then at 40 °C for 3 h. To the resulting solution was added dropwise 30 mL of water, followed by stirring at 40 °C for 3 h. After distillation, the residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was removed at reduced pressure. The liquid residue was fractionally distilled off (6 Torr, 100 °C) in vacuo to yield 15.3 g of brown viscous liquid (52.4%). ^1H NMR (DMSO-d_6): $\delta = 7.52$ (d, 1 H), 7.45 (d, 1 H), 7.33 (d, 1 H), 7.09 (t, 1 H), 6.98 (t, 1 H), 6.39 (d, 1 H), 4.87 (t, 1 H), 4.22 (t, 2 H), 3.70 (t, 2 H). IR (KBr): 3378 (ν_{O-H}), 2933 and 2878 cm^{-1} ($\nu_{\text{aliphatic C-H}}$).

2-(1*H*-1-Indolyl)ethyl Acetate (2). A stirred solution of 14.5 g (90.0 mmol) of **1** in 100 mL of acetic anhydride was heated at reflux for 2 h. After cooling, the solvent was distilled off in vacuo. The liquid residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was removed at reduced pressure. The liquid residue was chromatographed on a silica gel column (ethyl acetate:*n*-hexane = 1:4) and the solvent of the first fraction was removed at reduced pressure to yield 12.7 g of brown viscous liquid (69.4%). ^1H NMR (DMSO-d_6): $\delta = 7.54-7.45$ (m, 2 H), 7.35 (d, 1 H), 7.12 (t, 1 H), 7.04 (t, 1 H), 6.42 (d, 1 H), 4.41 (t, 2 H), 4.29 (t, 2 H), 1.90 (s, 3 H). IR (KBr, cm^{-1}): 1740 ($\nu_{\text{C=O of ester}}$).

2-(3-Formyl-1*H*-1-indolyl)ethyl Acetate (3). To a stirred solution of 12.7 g (62.5 mmol) of **2** in 250 mL of dry DMF was added dropwise 14.6 mL (157 mmol) of phosphorus oxychloride at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at 100 °C for 2 h. After cooling, the solution was poured into water. The resulting mixture was neutralized to pH 7 with 2 N NaOH and extracted with dichloromethane. The extract was dried with $MgSO_4$, and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate:*n*-hexane = 1:1) and the solvent of the second fraction was removed at reduced pressure to produce 10.0 g of brown viscous liquid (69.2%). ^1H NMR (DMSO-d_6): $\delta = 9.89$ (s, 1 H), 8.34 (s, 1 H), 8.10 (d, 1 H), 7.64 (d, 1 H), 7.36−7.18 (m, 2 H), 4.56 (t, 2 H), 4.37 (t, 2 H), 1.95 (s, 3 H). IR (KBr): 2814 and 2758 ($\nu_{\text{C-H of aldehyde}}$), 1740 ($\nu_{\text{C=O of ester}}$), 1660 cm^{-1} ($\nu_{\text{C=O of aldehyde}}$).

1-(2-Hydroxyethyl)-1*H*-3-indolecarbaldehyde (4). A stirred solution of 5.00 g (21.6 mmol) of **3** and 2.43 g (43.2 mmol) of potassium hydroxide in 30 mL of ethanol was heated at reflux for 2 h. After cooling, the solvent was removed at reduced pressure. The solid residue was washed with water, filtered, and dried. Recrystallization from ethanol yielded 3.50 g of an orange needle-shaped crystal (85.6%). Mp: 136 °C. ^1H NMR (DMSO-d_6): $\delta = 9.91$ (s, 1 H), 8.26 (s, 1 H), 8.12 (d, 1 H), 7.62 (d, 1 H), 7.34−7.20 (m, 2 H), 5.05 (t, 1 H), 4.31 (t, 2 H), 3.74 (t, 2 H). IR (KBr): 3478 (ν_{O-H}), 2831 and 2770 ($\nu_{\text{C-H of aldehyde}}$), 1643 cm^{-1} ($\nu_{\text{C=O of aldehyde}}$).

6-(1*H*-1-Indolyl)-1-hexanol (5). A 59.4 g (1060 mmol) sample of powdered potassium hydroxide was stirred for 10 min in 200 mL of dry DMF. Then, 25.0 g (213 mmol) of indole was added slowly and stirred for 1 h. After addition of 34.8 g (255 mmol) of 6-chlorohexanol, the solution was stirred at room temperature for 4 h and then at 40 °C for 12 h. The resulting mixture was poured into water and extracted with ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was removed at reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 1:1) to yield 20.3 g of brown viscous liquid (43.9%). ^1H NMR ($CDCl_3$): $\delta = 7.62$ (d, 1 H), 7.32 (d, 1 H), 7.19 (t, 1 H), 7.11−7.06 (m, 2 H), 6.48 (d, 1 H), 4.10 (t, 2 H), 3.57 (t, 2 H), 1.89−1.78 (m, 2 H), 1.53−1.41 (m, 2 H), 1.40−1.28 (m, 4 H). IR (KBr): 3454 (ν_{O-H}), 2945 and 2860 ($\nu_{\text{aliphatic C-H}}$).

6-(1*H*-1-Indolyl)hexyl Acetate (6). This compound was synthesized from **5** by the same procedure as described for compound **2** (brown viscous liquid, 98.5%). ^1H NMR ($CDCl_3$): $\delta = 7.63$ (d, 1 H), 7.33 (d, 1 H), 7.20 (t, 1 H), 7.12−7.07 (m, 2 H), 6.49 (d, 1 H), 4.12 (t, 2 H), 4.02 (t, 2 H), 2.02 (s, 3 H), 1.89−1.81 (m, 2 H), 1.59−1.56 (m, 2 H), 1.36−1.32 (m, 4 H). IR (KBr): 1734 cm^{-1} ($\nu_{\text{C=O of ester}}$).

6-(3-Formyl-1*H*-1-indolyl)hexyl Acetate (7). This compound was synthesized from **6** by the same procedure as described for compound **3** (brown viscous liquid, 62.0%). ^1H NMR ($CDCl_3$): $\delta = 9.95$ (s, 1 H), 8.30 (m, 1 H), 7.67 (s, 1 H), 7.40−7.27 (m, 3 H), 4.15 (t, 2 H), 4.04 (t, 2 H), 2.03 (s, 3 H), 1.99−1.89 (m, 2 H), 1.64−1.57 (m, 2 H), 1.40−1.37 (m, 4 H). IR (KBr): 2808 and 2754 ($\nu_{\text{C-H of aldehyde}}$), 1734 ($\nu_{\text{C=O of ester}}$), 1658 cm^{-1} ($\nu_{\text{C=O of aldehyde}}$).

1-(6-Hydroxyhexyl)-1*H*-3-indolecarbaldehyde (8). This compound was synthesized from **7** by the same procedure as described for compound **4** (brown viscous liquid, 89.1%). ^1H NMR ($CDCl_3$): $\delta = 9.96$ (s, 1 H), 8.31−8.27 (m, 1 H), 7.71 (s, 1 H), 7.39−7.27 (m, 3 H), 4.17 (t, 3 H), 3.62 (t, 2 H), 1.95−1.88 (m, 2 H), 1.57−1.53 (m, 2 H), 1.51−1.40 (m, 4 H). IR (KBr): 3408 (ν_{O-H}) 2812 and 2756 ($\nu_{\text{C-H of aldehyde}}$), 1656 cm^{-1} ($\nu_{\text{C=O of aldehyde}}$).

2−3-[(*E*)-2-(4-Nitrophenyl)-1-ethenyl]-1*H*-1-indolyl-1-ethanol (IDS2). A 2.70 g (14.3 mmol) sample of **4** and 2.80 g (15.4 mmol) of 4-nitrophenyl acetic acid were dissolved in 60 mL of absolute ethanol. The solution was heated at 60 °C and treated with a solution of 2.85 mL (28.8 mmol) of piperidine in 5 mL of ethanol. The reaction mixture was heated at reflux for 36 h. After cooling, the solvent was removed at reduced pressure, and the resulting solid was washed with water and dried. Recrystallization from ethanol yielded 1.84 g of dark red crystals (41.7%). mp: 195 °C. ^1H NMR ($CDCl_3$): $\delta = 8.15$ (d, 2 H), 8.09 (d, 1 H), 7.80 (d, 2 H), 7.78 (s, 1 H), 7.72 (d, 1 H; $J_{\text{trans}} = 16.6$ Hz), 7.54 (d, 1 H), 7.26−7.13 (m, 3 H), 5.00 (t, 1 H), 4.24 (t, 2 H), 3.75 (t, 2 H). IR (KBr): 3467 (ν_{O-H}), 1528 and 1333 cm^{-1} ($\nu_{\text{nitro group}}$).

(*Z*)-2-[1-(2-Hydroxyethyl)-1*H*-3-indolyl]-1-(4-nitrophenyl)-1-ethenyl Cyanide (IDC2). A 3.00 g (15.9 mmol) sample of **4** and 2.70 g (16.7 mmol) of 4-nitrophenyl acetonitrile were dissolved in 60 mL of absolute ethanol. The solution was heated at 60 °C and treated with a solution of 3.20 mL (32.3 mmol) of piperidine in 5 mL of ethanol. The reaction mixture was heated at reflux for 12 h. As the reaction progressed, the product precipitated from the solution. After cooling, the precipitated product was filtered, washed with water and dried. Recrystallization from ethanol yielded 5.00 g of dark red crystal (94.3%). Mp: 225 °C. ^1H NMR (DMSO-d_6): $\delta = 8.47$ (s, 1 H), 8.41 (s, 1 H), 8.20 (d, 2 H), 8.11 (d, 1 H), 7.95 (d, 2 H), 7.58 (d, 1 H), 7.34−7.20 (m, 2 H), 5.06 (t, 1 H), 4.34 (t, 2 H), 3.74 (t, 2 H). IR (KBr): 3516 (ν_{O-H}), 2209 ($\nu_{\text{nitrile group}}$), 1518 and 1345 cm^{-1} ($\nu_{\text{nitro group}}$).

6−3-[(*E*)-2-(4-Nitrophenyl)-1-ethenyl]-1*H*-1-indolyl-1-hexanol (IDS6). This compound was synthesized from **8** by the same procedure as described for compound **IDS2** (red viscous liquid, 39.3%). ^1H NMR (DMSO-d_6): $\delta = 8.18$ (d, 2 H), 8.08 (d, 1 H), 7.81 (t, 3 H), 7.70 (d, 1 H), 7.53 (d, 1 H), 7.26−7.17 (m, 3 H), 4.36 (t, 1 H), 4.19 (t, 2 H), 1.79−1.74 (m, 2 H), 1.37−1.27 (m, 6 H). IR (KBr): 3332 (ν_{O-H}), 1490 and 1326 cm^{-1} ($\nu_{\text{nitro group}}$).

2−3-[(*E*)-2-(4-Nitrophenyl)-1-ethenyl]-1*H*-1-indolylethyl 2-Methyl Acrylate (MAcIDS2). A 1.50 g (4.86 mmol) sample of **IDS2** and 2.00 mL (14.4 mmol) of triethylamine were dissolved in mixed solvent (dichloromethane 50 mL/DMF 10 mL) at 0 °C. The solution was treated under nitrogen atmosphere with a solution of 1.40 mL (14.4 mmol) of methacryloyl chloride in 15 mL of dichloromethane. The reaction mixture was heated at reflux for 6 h. After cooling, the solvent was removed at reduced pressure and the residue was poured into water. The resulting solid was filtered and chromatographed on a silica gel column (ethyl acetate:*n*-hexane = 1:1). The solvent of the first fraction was removed at reduced pressure to yield 1.46 g of solid monomer (79.7%). ^1H NMR ($CDCl_3$): δ

$= 8.16$ (d, 2 H), 8.09 (d, 1 H),7.80 (s, 1 H), 7.79 (d, 2 H), 7.69 (d, 1 H; $J_{trans} = 16.5$ Hz), 7.59 (d, 1 H), 7.28−7.14 (m, 3 H), 5.89 (s, 1 H), 5.58 (s,1 H), 4.52 (t, 2 H), 4.40 (t, 2 H), 1.74 (s, 3 H). IR (KBr): 1717 ($\nu_{C=O\ of\ ester}$), 1508 and 1335 cm^{-1} ($\nu_{nitro\ group}$).

2−3-[(*Z*)-2-Cyano-2-(4-nitrophenyl)-1-ethenyl]-1*H*-1-indolylethyl 2-Methyl Acrylate (MAcIDC2). This monomer was prepared from 4.50 g (13.5 mmol) of **IDC2**, 5.63 mL (40.5 mmol) of triethylamine, and 3.95 mL (40.5 mmol) of methacryloyl chloride in mixed solvent (dichloromethane 80 mL/DMF 20 mL) by the same procedure as described for **MACIDS2** (4.60 g, 84.9%). mp: 218 °C. ^{1}H NMR (CDCl$_3$): $\delta = 8.54$ (s, 1 H), 8.49 (s, 1 H), 8.28 (d, 2 H), 8.16 (d, 1 H), 8.04 (d, 2 H), 7.79 (d, 1 H), 7.36−7.23 (m, 2 H), 5.94 (s, 1 H), 5.61 (s, 1 H), 4.70 (t, 2 H), 4.45 (t, 2 H), 1.78 (s, 3 H). IR (KBr): 2212 ($\nu_{nitrile\ group}$), 1707 ($\nu_{C=O\ of\ ester}$), 1518 and 1331 cm^{-1} ($\nu_{nitro\ group}$).

6−3-[(*E*)-2-(4-Nitrophenyl)-1-ethenyl]-1*H*-1-indolylhexyl Acrylate (AcIDS6). This compound was prepared from 1.50 g (4.12 mmol) of **IDS6**, 1.71 mL (12.3 mmol) of triethylamine, and 1.00 mL (12.3 mmol) of acryloyl chloride in dichloromethane (20 mL) by the same procedure as described for **MAcIDS2** (1.00 g, 58.0%). ^{1}H NMR (CDCl$_3$): $\delta = 8.20$ (d, 2 H), 7.99 (d, 1 H), 7.60 (d, 2 H), 7.50 (d, 1 H), 7.39−7.24 (m, 4 H), 7.12 (d, 1 H), 4.15 (q, 4 H), 1.92−1.87 (m, 2 H), 1.69−1.62 (m, 2 H), 1.42−1.26 (m, 4 H). IR (KBr): 1704 ($\nu_{C=O\ of\ ester}$), 1490 and 1330 cm^{-1} ($\nu_{nitro\ group}$).

Polymerization. P1 (Copolymer of MAcIDS2 with Methyl Methacrylate). A 0.940 g (2.50 mmol) sample of **MAcIDS2**, 0.250 g (2.50 mmol) of distilled methyl methacrylate (**MMA**), and 0.040 g (5 mol %) of 2,2′azobis(isobutyronitrile) (AIBN) were dissolved in 10 mL of *N*-methylpyrrolidinone (NMP). The solution was degassed by standard vacuum/freeze/thaw technique and heated in a sealed ampule at 65 °C for 48 h. After cooling, the resulting solution was diluted to twice its original volume with tetrahydrofuran (THF) and poured into 200 mL of vigorously stirred methanol to precipitate the polymer. Purification was carried out by repeated reprecipitation from THF into methanol until no monomer was observed in the TLC plate. Finally, 0.950 g of pure copolymer **P1** was obtained (80.0%).

P2 (Copolymer of MAcIDC2 with Methyl Methacrylate). Copolymer **P2** was synthesized from a solution of 1.00 g (2.50 mmol) of **MAcIDC2**, 0.250 g (2.50 mmol) of distilled **MMA**, and 0.040 g (5 mol %) of AIBN in 20 mL of NMP by the same procedure of the synthesis of **P1**. A 0.930 g yield of **P2** was obtained (74.4%).

P3 (Copolymer of AcIDS6 with Butyl Acrylate). Copolymer **P3** was synthesized from a solution of 0.500 g (1.19 mmol) of **AcIDS6**, 0.460 g (3.58 mmol) of distilled butyl acrylate, and 0.039 g (5 mol %) of AIBN in 5 mL of NMP by the same procedure for the synthesis of **P1**. A 0.550 g yield of **P3** was obtained (57.3%).

Synthesis of Photoconducting Plasticizer. 9-(2-Ethylhexyl)-9*H*-carbazole (9). A 13.5 g (240 mmol) sample of powdered potassium hydroxide was dispersed in 350 mL of DMF at room temperature, and 20 g (120 mmol) of carbazole was added slowly. After the mixture was stirred for 1 h, 35 g (180 mmol) of 1-bromo-2-ethylhexane was added dropwise, and the reaction was stirred overnight at room temperature. The resulting solution was poured into water, and the crude product was extracted with ethyl acetate. The solution was washed with brine and water and dried with MgSO$_4$. The solvent was removed at reduced pressure and residual liquid was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/10) to yield a yellowish viscous liquid (98%). ^{1}H NMR (CDCl$_3$): $\delta = 8.09$ (d, 2 H), 7.48−7.37 (m, 4 H), 7.22 (t, 2 H), 4.15 (d, 2 H), 2.10 (m, 1 H), 1.43−1.22 (m, 8 H), 0.93−0.83 (m, 6 H). IR (KBr window, cm^{-1}): 3060 ($\nu_{aromatic\ C-H}$), 2960, 2930 and 2880 ($\nu_{aliphatic\ C-H}$).

9-(2-Ethylhexyl)-9*H*-carbazole-3-carbaldehyde (10). This compound was synthesized from 2.5 g (8.9 mmol) of **9**, 3.46 mL (44.7 mmol) of dry DMF, and 2.08 mL (22.4 mmol) of phosphorus oxychloride by the same procedure as described for **3** and purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to yield 2.75 g of liquid product (98%). ^{1}H NMR (CDCl$_3$): $\delta = 10.13$ (s, 1 H), 8.54 (s, 1 H), 8.14 (d, 1 H), 7.98 (d, 1 H), 7.51−7.25 (m, 4 H), 4.14 (d, 2 H), 2.03 (m, 1 H), 1.43−1.11 (m, 8 H), 0.93−0.70 (m, 6 H). IR (KBr window, cm^{-1}): 2810 and 2720 ($\nu_{C-H\ of\ aldehyde}$), 1690 ($\nu_{C=O\ of\ aldehyde}$).

***N*′-[9-(2-Ethylhexyl)-9*H*-carbazole-3-ylmethylene]-*N*,*N*-diphenylhydrazine (EHCzHy).** To a magnetically stirred solution of 1,1-diphenylhydrazine hydrochloride (2.37 g, 10.7 mmol) in 40 mL of ethanol was added sodium acetate trihydrate (2.44 g, 17.9 mmol) at room temperature. Then a solution of **10** (2.75 g, 8.9 mmol) in 40 mL of ethanol was added dropwise for 30 min. After the mixture was stirred 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 with MgSO$_4$. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/10) to yield 3.6 g of viscous liquid (85%). ^{1}H NMR (CDCl$_3$): $\delta = 8.19$ (s, 1 H), 8.07 (t, 1 H), 7.89 (q, 1 H), 7.47−7.34 (m, 8 H), 7.27−7.17 (m, 7 H), 4.12 (d, 2 H), 2.04 (m, 1 H), 1.42−1.27 (m, 8 H), 0.93−0.70 (m, 6 H). IR (KBr): 1597 cm^{-1} ($\nu_{C=N}$).

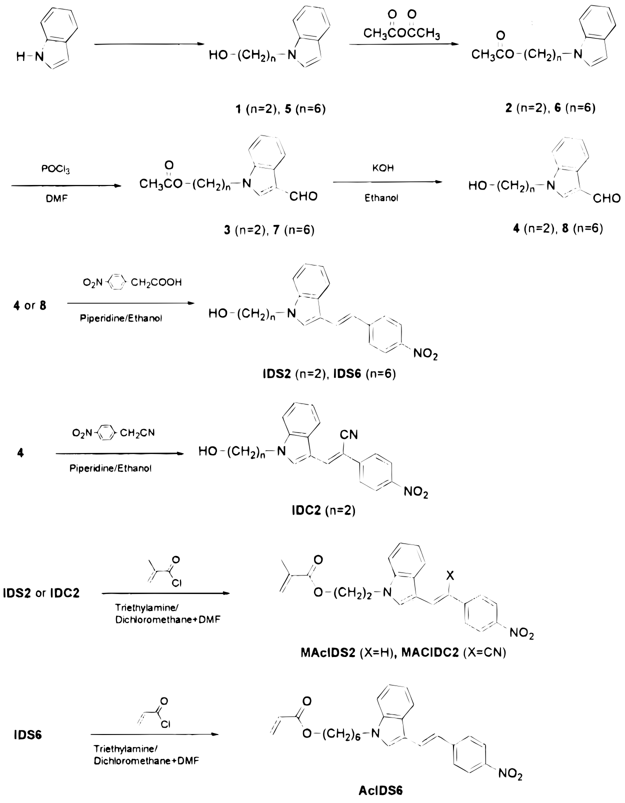
Film Fabrication. For the electrooptic and second-harmonic generation measurements, thin polymer films of **P1** and **P2** were prepared. Polymers were dissolved in dichloroethane and the solutions were filtered with a Teflon membrane filter (Millipore, 0.22 μm). Polymer films were spin coated at 2000 rpm onto slide glass and indium−tin−oxide- (ITO-) coated glass. Residual solvent was removed by heating the films in a vacuum oven for 2 days. The thickness of the thin films was monitored with TENCOR P-10 profilometer.

The thick film of **P3**, which was used in photorefractivity measurements, was obtained as follows. Proper amounts of copolymer **P3**, with specified amount of 2,4,7-trinitro-9-fluorenone (TNF) and photoconducting plasticizer (**EHCzHy**) were dissolved in dichloromethane. The solution was filtered through a membrane filter and then cast onto ITO-coated glass at room temperature and dried at 90 °C for 12 h to remove the solvent. This film was pressed at 80 °C to 100 μm thickness by the use of a Teflon spacer and an additional ITO-coated glass plate. Finally, to protect the sample from moisture, this whole assembly was encapsulated with epoxy adhesive before connecting the lead wires.

Electrooptic (EO) Measurement. A gold electrode was sputter-coated over the polymer film which was previously spin-coated onto ITO glass. To align the chromophores in polymer film, contact poling was carried out. The film was heated around T_g, and then poling fields of 20, 40, and 70 V/μm were applied to the gold electrode. After 15 min, the sample was cooled rapidly to about 30 °C, at which point the poling field was removed. Directly after poling, the EO measurement was carried out. The EO coefficient (r_{33}) of poled polymer was measured at the wavelength of 633 nm (He−Ne laser) using a simple reflection method.[20] A Soleil-Babinet compensator was used to bias the optical interference signal to the half-maximum intensity. The amplitude of modulated intensity was determined using a lock-in amplifier, which was used to calculate the r_{33} values.[20] Refractive indices of **P1** and **P2** were measured by the prism coupling method using polymer films on glass.

Second-Harmonic Generation (SHG) Measurement. A corona poling process was utilized for the preparation of noncentrosymmetric polymer films for the SHG measurement. Polymer film spin-coated onto a glass substrate was affixed to an aluminum plate equipped with a cartridge heater. Polymer film was heated around T_g, and then the poling voltage of 5 kV was applied through a thin tungsten wire electrode. After 15 min, the film was cooled rapidly to about 30 °C, at which point the poling field was removed. For the SHG measurement, which was carried out immediately after poling, Q-switched Nd:YAG laser ($\lambda = 1064$ nm) with pulse width of 10 ns and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. SHG coefficients d_{33} and d_{31} were derived from the analysis of measured Maker-fringes.[21]

Scheme 1. Synthesis of Chromophores and Monomers



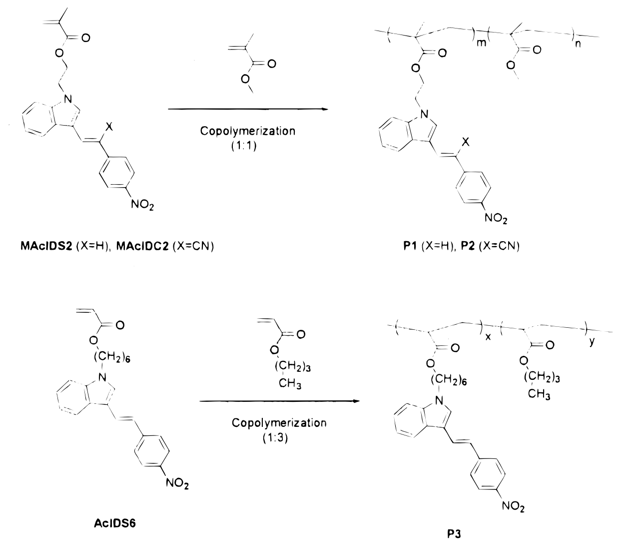
Photoconductivity Measurement. The dark- and the photoconductivities of polymer films were evaluated by measuring a current through the polymer film sandwiched between gold and ITO using a Keithley 617 electrometer. A visible light source, 3M XL 1000, having an emitting region of 390–510 nm and a maximum emitting intensity at 485 nm, and a He–Ne laser were utilized for the photoconductivity measurement. 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.

Photorefractivity Measurement. The photorefractive property of a 100 μm-thick film of low T_g polymer **P3** was determined by two-beam coupling (TBC) and degenerated four-wave mixing (FWM) experiments. We employed the tilted setup to carry out the experiment. The normal of the sample surface was tilted 60° with respect to the symmetric axis of the two intersected beams, and external interbeam angle was 11°. In two-beam coupling, two mutually coherent p-polarized He–Ne laser beams with equal power of 30 μW at a wavelength of 633 nm were incident upon the sample. Using two beams of equal intensity, the photorefractive gain could be estimated from[22]

$$\Gamma = (1/L)[\ln(\gamma_0) - \ln(2 - \gamma_0)]$$

where L is the path length of the beam through the sample and γ_0 is the beam coupling ratio between the two writing beams. For four-wave mixing, two s-polarized beams with the intensity of 60.7 mW/cm^2 were used as the writing beams and the p-polarized one with the intensity of 1.27 mW/cm^2 counterpropagated to one of the writing beams as a reading beam. Diffraction efficiency was determined by the ratio of the intensity of diffracted signal to that of incident reading beam. And the response time of the grating decay was measured as follows. After the diffraction efficiency reached the steady-state, one of writing beam was turned off, and the decay of the diffraction efficiency was fitted with an exponential function of the form $\eta(t) = \eta_0[\exp(-t/\tau)]^2$, where η_0 is the steady-state diffraction efficiency.

Scheme 2. Synthesis of Polymers



Results and Discussion

Synthesis of Multifunctional Chromophores and Monomers. The reaction pathway to the synthesis of indole-based multifunctional photorefractive chromophores is illustrated in Scheme 1. Briefly, the chromophores were synthesized by the Knoevenagel reaction of aldehyde derivatives bearing indole as an electron donating group with 4-nitrophenylacetic acid or 4-nitrophenylacetonitrile. The aldehyde derivatives **4** and **8** were prepared in four steps, i.e., introduction of spacer group, protection of hydroxy group, Vilsmeier formylation, and deprotection.

The chromophore **IDS6**, which was specifically designed to synthesize low T_g copolymer **P3** for photorefraction, exhibited excellent solubility compared to other chromophores presumably due to the long alkyl spacer. As for the synthesis, however, the α-cyanonitrostilbene derivative (**IDC2**), which was synthesized from compound **4** and 4-nitrophenylacetonitrile, was obtained in a higher yield ($Y = 94\%$) than the nitrostilbene derivatives ($Y = 41.7$ and 39.3% for **IDS2** and **IDS6**, respectively). This is presumably due to the increased extent of carbanion formation by the more electron-withdrawing cyano group and the poor solubility of the α-cyanonitrostilbene derivative, which possibly acted as a driving force of the forward reaction through precipitation in a reversible reaction. Monomers were easily prepared by the reaction of the chromophores with methacryloyl chloride and acryloyl chloride. The absorption peaks of the carbonyl group at 1717 cm^{-1} and nitro group at 1508 and 1335 cm^{-1} were observed in the IR spectrum of **MAcIDS2**. The chemical shifts of *trans*-stilbene protons at 7.69 and 7.21 ppm, vinyl protons at 5.94 and 5.61 ppm, and methylene protons of the spacer at 4.46 and 3.34 ppm could successfully be assigned in the NMR spectrum of **MAcIDS2**. The structure of **AcIDS6** was similarly identified by spectroscopic means. The IR and NMR spectra of **MAcIDC2** are similar to those of **MAcIDS2**, but the stretching band of the nitrile group was identified at 2212 cm^{-1} in IR spectrum and the chemical shift of the β proton of α-cyanostilbene was characterized at 8.54 ppm in the NMR spectrum.

Synthesis and General Properties of Copolymers. Three different polymers were obtained by free

Table 1. Results of Copolymerization

polymer	m_{feed}	$m_{\text{pol.}}$	yield (%)	$M_n{}^d$	$M_w{}^d$	M_w/M_n
P1	1:1[a]	1:1.85[b]	80.0	7530	19500	2.59
P2	1:1[a]	1:2.31[b]	74.4	6490	13700	2.11
P3	1:3[c]		57.3	2560	7250	2.83

[a] Mole ratio of multifunctional monomer: MMA in the feed. [b] Mole ratio of multifunctional monomer: MMA in copolymer measured by the extinction coefficient of the UV−vis absorption [c] Mole ratio of multifunctional monomer:butyl acrylate in the feed. [d] Measured by GPC in THF using polystyrene standards.

Table 2. Properties of High T_g Nonlinear Optical Copolymers

polymer	T_g (°C)	$\lambda_{\max}{}^a$	$\lambda_{\text{cutoff}}{}^a$	$d_{33\,(\text{pm/V})}{}^b$	$d_{31(\text{pm/V})}{}^b$	d_{33}/d_{31}
P1	152	422	540	49 (0.24[c])	16	3.1
P2	145	420	526	17 (0.22[c])	5.9	2.9

[a] Film. [b] Second-harmonic generation coefficient. [c] Order parameter $\Phi = 1 - A_p/A_0$, where A_p is the absorption intensity of poled film and A_0 is the absorption intensity of unpoled film.

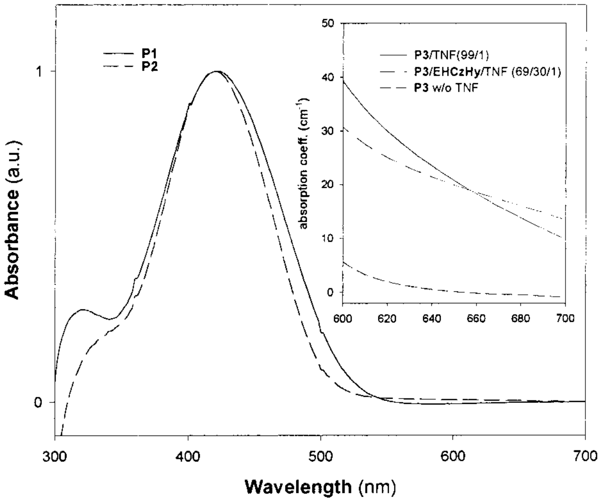


Figure 1. UV−vis absorption spectra of copolymers **P1** and **P2** (inset: absorption coefficients of photorefractive **P3** composite).

Table 3. Calculated Values of Chromophores by MOPAC 6

	$\mu_{(\text{Debye})}{}^a$	$\alpha_{(10^{-23}\text{esu})}{}^b$	$\beta_{(10^{-30}\text{esu})}{}^c$
IDS2	6.21	8.6	32.6
IDC2	6.47	8.6	25.3
PDCST	5.66	4.62	19.1

[a] Dipole moment. [b] Polarizability. [c] First hyperpolarizability.

radical copolymerization of the multifunctional monomers (**MAcIDS2, MAcIDC2, AcIDS6**) with methyl methacrylate or butyl acrylate as shown in Scheme 2. Copolymerization was effected in *N*-methylpyrrolidinone solution at 65 °C for 2 days using AIBN as initiator. The results of copolymerization and the molecular weights of obtained copolymers are shown in Table 1. Because the monomer containing the α-cyanostilbene derivative (**MAcIDC2**) had a relatively poor solubility compared to **MAcIDS2**, the polymerization of **P2** was carried out in larger amount of solvent. Both the copolymers **P1** and **P2** were soluble in various solvents such as THF, chloroform, DMF, and dichloroethane but were partially soluble in dichloromethane. The molecular weight of polymers, determined by gel permeation chromatography, was $M_w = 19\,500$ and $M_w/M_n = 2.59$ for **P1** and $M_w = 13\,700$ and $M_w/M_n = 2.11$ for **P2**. With the feeding mole ratio of 1:1 (multifunctional monomer: **MMA**), the resultant mole ratios of each component in the copolymers were estimated to be 1:1.85 for **P1** and 1:2.31 for **P2** through the quantitative analysis of the UV−vis absorption spectra. Table 2 summarizes the thermal, optical, and nonlinear optical properties of methacrylate copolymers. As shown in Figure 1, the absorption maxima of the $\pi-\pi^*$ transition of chromophores were 422 nm for **P1** and 420 nm for **P2**, respectively, with apparent cutoff at ca. 540 nm. The DSC thermograms of **P1** and **P2** showed that these polymers were amorphous in nature and exhibited glass transitions at about 150 °C, which was attributed to the rigidity of the short spacer group in the chromophores. The initial decomposition temperatures of the polymers were as high as 290 °C. Polymers **P1** and **P2** showed excellent optical transparency; however, it was difficult to fabricate a 100 μm thick film for photorefractive experiment from these high T_g polymers. To overcome these limitations of **P1** and **P2**, copolymer **P3** with a much lower T_g was designed and synthesized. To increase the free volume in the polymer matrix, a longer alkyl chain (hexyl group) was introduced to the chromophore (**IDS6**). In addition, the monomer (**AcIDS6**) was obtained by the reaction of **IDS6** with acryloyl chloride, instead of methacryloyl chloride, and, finally, copolymerized with butyl acrylate (**BA**) at a composition of 1:3 (**AcIDS6:BA**). As expected, T_g of the synthesized copolymer **P3** was measured to be 8 °C.

NLO Properties of Copolymers. The dipole moment (μ), polarizability (α), and first hyperpolarizability (β) of **IDS2** and **IDC2**, calculated by MOPAC 6 using a PM3 Hamiltonian, are listed in Table 3. First hyperpolarizability, which is related to second-order NLO property of chromophore, was 32×10^{-30} esu for **IDS2** and 25×10^{-30} esu for **IDC2**. Because these chromophores possess a much higher β value than the well-known multifunctional photorefractive chromophore, 4-piperidinobenzylidenemalonitrile (**PDCST**), it was thought that our indole-based chromophores had enough NLO properties to give the photorefractive effect. The refractive indices of **P1** and **P2** were measured to be 1.693 and 1.686, repectively, and the EO coefficients (r_{33}) of **P1** and **P2** at 633 nm He−Ne laser were in the range of 8∼11 pm/V when polymer films were poled by the electric field of 70 V/μm at around T_g for 15 min. This fast poling behavior of indole-based polymers at lower electric fields is compared with that of a tricyanovinylcarbazole-based polymer,[23] which showed an electrooptic coefficient of 6.1 pm/V after poling by the electric field of 100 V/μm at around T_g for 8 h. We also reported the poling difficulty of NLO polymers containing a carbazole-based multifunctional chromophore.[14−16] The electrooptic coefficients of **P1** and **P2** increased linearly with poling electric field as shown in Figure 2.

SHG coefficients (d_{33}) of corona-poled polymer films were measured to be 49 pm/V for **P1** and 17 pm/V for **P2** as shown in Table 2. Considering that λ_{cutoff} was 540 nm for **P1** and 526 nm for **P2**, these values are considered to be virtually nonresonant ones.

The temporal stability of NLO activity was investigated by monitoring the decay of EO coefficient as a function of time at elevated temperature, 80 °C. After the initial fast reduction, EO coefficient of **P1** was very much stabilized to about 76% of its initial value. (Figure 3) Compared with the temporal stability of well-known NLO methacrylate polymer containing dimethylaminonitrostilbene (**P2ANS**; see Figure 3), excellent temporal stability of **P1** was indirectly proved.

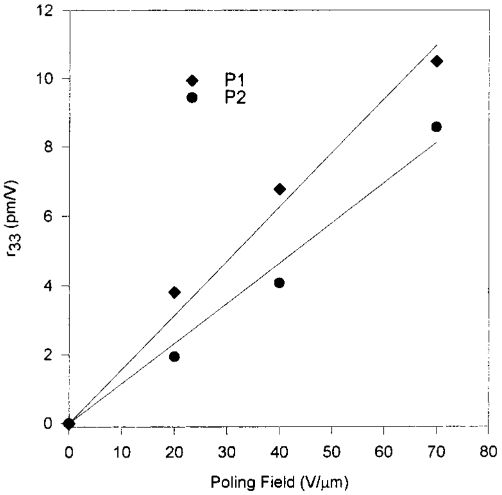


Figure 2. Electrooptic coefficients of copolymers **P1** and **P2**.

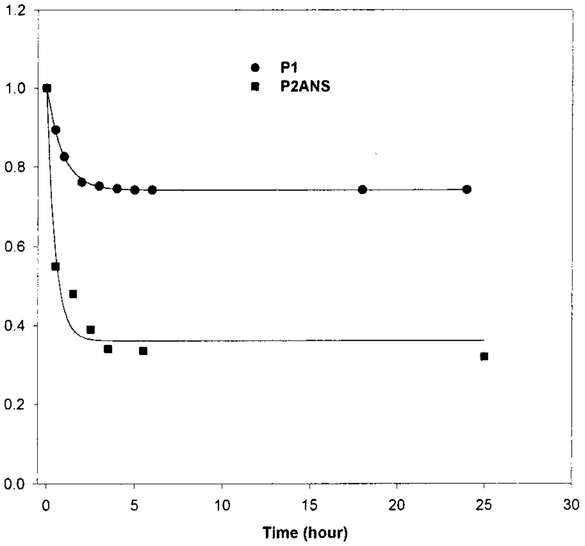


Figure 3. Temporal stability of electrooptic coefficients at 80 °C.

Photoconductivity. When the visible light of 0.8 mW·cm^{-2} intensity was irradiated on the polymer films **P1** and **P2**, current density increased remarkably even through we did not add any sensitizer or transporting agent. Photoconductivities were estimated to be 1.72 × 10^{-12} and 2.69 × 10^{-13} S·cm^{-1} at a field of 40 V/μm for **P1** and **P2**, respectively. The conductivity values under illumination were more than an order of magnitude larger than those of in dark. It was also noted that **P1** had higher photoconductivity than **P2**, because of the more effective conjugation due to its planar structure. The electric field dependence of photoconductive sensitivity (photoconductivity per unit light intensity) is shown in Figure 4. As expected, the photoconductive sensitivity increased with electric field strength. At about 0.4 MV/cm, the photoconductive sensitivities were found to be 2.17 and 3.39 × 10^{-10} S·cm^{-1}/mW·cm^{-2} for **P1** and **P2**. From the above results, **P1** was considered to be the better candidate for the photorefractive polymer. In addition, He−Ne laser of 267 mW·cm^{-2} was used to determine the photoconductivity of **P1** at 633 nm where measurement of photorefractivity was carried out. Although **P1** did not exhibit increase of current density as irradiation of the light since it has no absorption at 633 nm, **P1** doped with TNF (1 wt %) showed distinct photoconductivity to be 4.0 × 10^{-12} S·cm^{-1} at the field of 87.5 V/μm. Its photoconductive sensitivity was 1.5 × 10^{-14} S·cm^{-1}/mW·cm^{-2} at the same electric field.

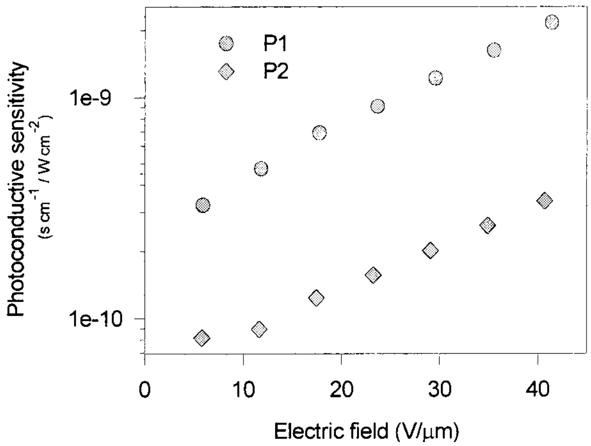


Figure 4. Photoconductive sensitivities of photoconducting NLO polymers.

Photorefractivity To investigate whether copolymer **P3** shows photorefractivity without the addition of any other NLO chromophores or charge transport materials, two photorefractive devices consisting of **P3** alone and **P3**/TNF (99/1 wt %), were fabricated. Absorption coefficients were measured to be 0.9 cm^{-1} for **P3** and 25.3 cm^{-1} for **P3**/TNF (99/1 wt %) at 633 nm, respectively, as shown in the inset of Figure 1. When TNF was doped, absorption coefficient at longer wavelength region increased significantly, which indirectly proves the formation of charge-transfer complex between **P3** and TNF, leading to the charge carrier generation at 633 nm. As expected, a device composed of **P3** alone did not show any detectable photorefractivity even at the electric field of 75 V/μm but a device composed of **P3**/TNF (99/1 wt %) showed a gain value of 2.2 cm^{-1} at 75 V/μm (Figure 5a) and a diffraction efficiency of 0.44% at 60 V/μm (Figure 7). This value is, though small, very meaningful because it is the first evidence that the newly synthesized indole-based chromophore and copolymer are multifunctional photorefractive materials.

We reported earlier that the introduction of carbazole hydrazone group into the copolymer structure enhanced the photoconductivity very significantly, but copolymerization with this bulk group led to the large increase of T_g.[16] In this work, we synthesized carbazole hydrazone with *N*-ethylhexyl substitution (**EHCzHy**) (Scheme 3), which formed a low T_g (22 °C) organic glass with excellent transparency and fluidity, and was expected to play the same level of photoconductivity, maintaining low T_g without crystallization. We consider that **EHCzHy** is an excellent photoconductive plasticizer, which will be utilized for the preparation of photorefractive polymer system even with high T_g multifunctional polymers. To demonstrate this possibility, we fabricated two photorefractive composite devices containing **EHCzHy**. The compositions were **P3**/**EHCzHy**/TNF (69/30/1 wt %) and **P3**/**EHCzHy**/TNF (49/50/1 wt %). The absorption coefficients at a wavelength of 633 nm were 25 cm^{-1} for the former and 18 cm^{-1} for the latter. Figure 5b displays the typical two-beam coupling behavior of **P3**/**EHCzHy**/TNF (49/50/1 wt %) at the electric field of 50 V/μm. The effect of electric field on the photorefractive two-beam coupling gain is shown in Figure 6. The gain increased superlinearly with electric field. The measured gain values of **P3**/**EHCzHy**/TNF (69/30/1 wt

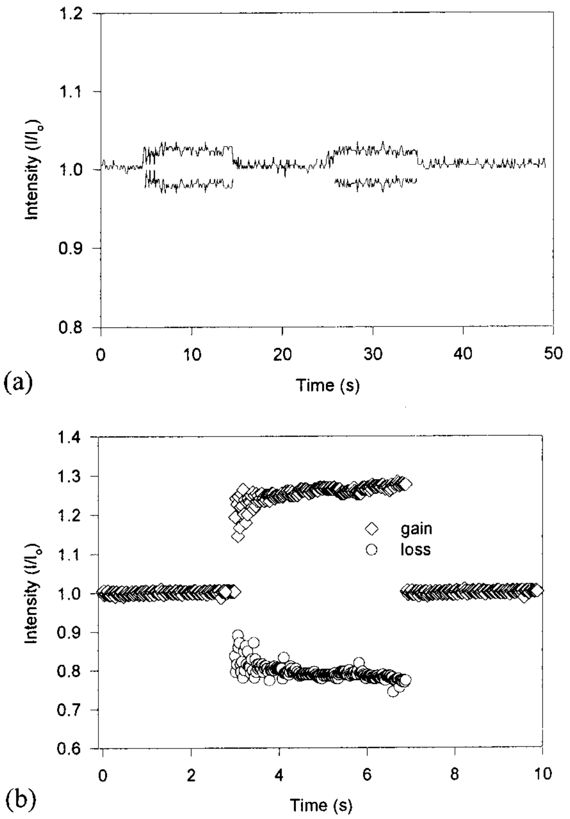


Figure 5. Energy transfer in two-beam coupling experiment of (a) **P3**/TNF(99/1) at 75 V/μm and (b) **P3**/**EHCzHy**/TNF(49/50/1) at 50 V/μm.

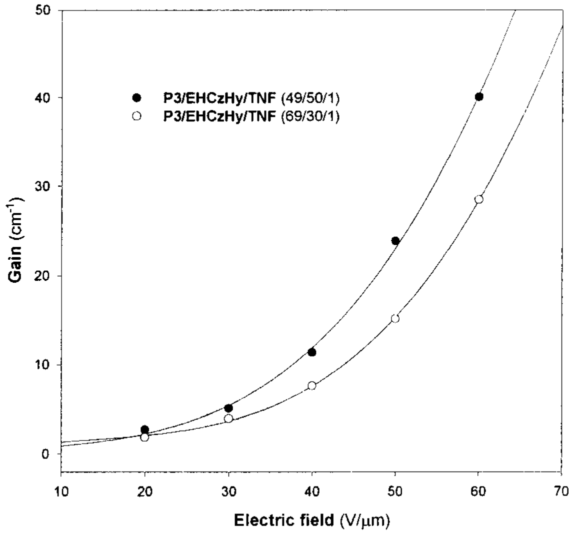


Figure 6. Effect of the electric field on the photorefractive two-beam coupling gain.

%) and **P3**/**EHCzHy**/TNF (49/50/1 wt %) were 27 and 40 cm^{-1}, with net gain values of 2 and 22 cm^{-1} at 60 V/μm, respectively.

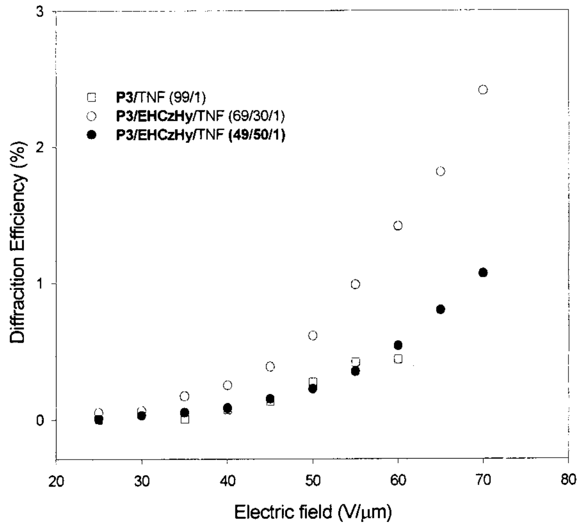


Figure 7. Effect of the electric field on the diffraction efficiency.

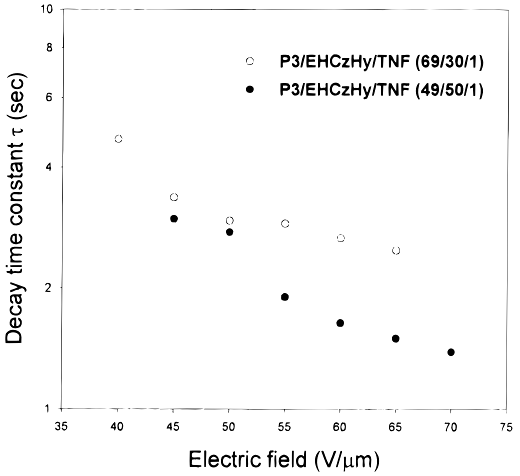
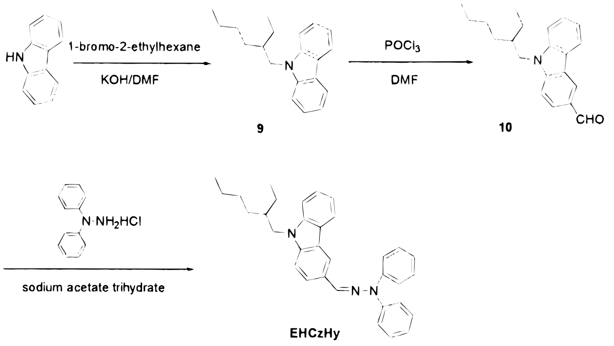


Figure 8. Effect of the electric field on the response time.

Scheme 3. Synthesis of Photoconducting Plasticizer (EHCzHy)



Figures 7 and 8 show the electric field dependence of steady-state diffraction efficiency and response time constant, respectively. The measured diffraction efficiencies of **P3**/**EHCzHy**/TNF (69/30/1 wt %) and **P3**/**EHCzHy**/TNF (49/50/1 wt %) were 2.41% and 1.07% at 70 V/μm. Response time constants of **P3**/TNF (99/1 wt %) were on the order of minutes, but they could be reduced by means of adding photoconducting plasticizer, **EHCzHy**, down to 1.39 s. Although the two-beam coupling gain and four-wave mixing response time were enhanced with the content of the photoconducting plasticizer (**EHCzHy**), diffraction efficiency seems to be somewhat reduced at higher plasticizer content as shown in Figure 7. More details of the photorefractivities and their correlation with the composition will be the subject of subsequent paper.

Conclusion

Novel multifunctional photorefractive chromophores and polymers containing indole as an electron donor group were newly synthesized. Fast and easy poling, large nonlinear optical coefficients (d_{33} as high as 49 pm/V), and distinct photoconductive sensitivity (on the order of 10^{-9} S·cm^{-1}/W·cm^{-2}) were identified with high T_g polymers **P1** and **P2**. Photorefractivity of these indole-based multifunctional polymers was demonstrated with low T_g copolymer, **P3**. **P3** doped with 1% TNF showed a two-beam coupling gain of 2.2 cm^{-1} at 75 V/μm and a diffraction efficiency of 0.44% at 60 V/μm. When the photoconducting plasticizer (**EHCzHy**) was added to **P3**, a net gain of 22 cm^{-1} and a diffraction efficiency of 2.41% could be achieved.

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