Notes

Low T_g Photorefractive Polyacrylate Containing 3-(6-Nitrobenzoxazol-2-yl)indole as a Monolithic Chromophore

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Introduction

Considerable attention has been paid to the photorefractive polymer with low glass transition temperature (T_g),[1−5] since Moerner et al. first reported outstanding photorefractivity of them.[6] It was suggested that the enhanced photorefractivity is attributed to the orientational enhancement in this low T_g polymer system.[7]

In our previous work, we reported syntheses and properties of high T_g photoconducting nonlinear optical (NLO) polymers containing 2-[3-(6-nitrobenzoxazol-2-yl)indol-1-yl]ethanol as a novel multifunctional chromophore.[8] Although the photoconductivity and NLO property of these indole−benzoxazole-based high T_g polymers were directly identified, photorefractivity of them was only demonstrated for the polymer composites containing photoconducting plasticizer. In this work, we report the synthesis and characterization of a low T_g photorefractive polymer containing the same monolithic chromophore with the aim to fully demonstrate the orientational enhancement and monolithic photorefractivity.

Experimental Section

Instruments. ^{1}H NMR spectra were recorded with the use of a Bruker AM-300 spectrometer. IR spectra were measured on a Midac FT-IR spectrophotometer. Mass spectrometer data were obtained from JMS AX505WA using electron impact (EI) mode. HP 8452-A 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 °C with Waters HPLC component system which was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out under nitrogen atmosphere on Perkin-Elmer DSC7 and Du Pont 2950, respectively.

Synthesis. Synthetic pathway to the photorefractive monomer, acrylic acid 6-[3-(6-nitrobenzoxazol-2-yl)indol-1-yl]hexyl ester (**M1**), and target polymer of this work (**P1**) is outlined in Scheme 1.

Synthesis of aldehyde derivative **3** was reported earlier by us.[9]

6-[3-(6-Nitrobenzoxazol-2-yl)indol-1-yl]hexan-1-ol (4). To a boiling solution of 2.0 g (6.96 mmol) of **3** in 20 mL of 1,2-dichlorobenzene was added 1.4 g (9.05 mmol) of 2-amino-5-nitrophenol under magnetic stirring. The reaction mixture was boiled for 2 h, and then the solvent was distilled off in a vacuum. The viscous residue was dissolved in 30 mL of dichloromethane. Under magnetic stirring, 3.06 g (6.96 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 100 mL of ethanol, and 0.78 g (13.9 mmol) of KOH was added. The solution was mildly heated with magnetic stirring for 1 h, and neutralized by HCl. After cooling, the precipitate was filtered and recrystallized from ethanol to yield 1.7 g of yellow solid (64%): mp 155 °C; ^{1}H NMR ($CDCl_3$) δ 8.46−8.43 (m, 2H; $J = 2.19$), 8.30 (q, 1H), 8.10 (s, 1H), 7.75 (d, 1H), 7.48−7.38 (m, 3H), 4.26 (t, 2H), 3.64 (t, 2H), 1.99−1.95 (m, 2H) 1.57−1.42 (m, 4H); IR (KBr pellet, cm^{-1}) 3360 (ν_{O-H}), 1590 and 1340 (ν_{nitro}).

Acrylic Acid 6-[3-(6-Nitrobenzoxazol-2-yl)indol-1-yl]-hexyl Ester (M1). To a magnetically stirred solution of 2 g (5.3 mmol) of **4** and 1.61 g (15.9 mmol) of triethylamine in 20 mL of dichloromethane was added 0.95 g (10.5 mmol) of acryloyl chloride dropwise at 0 °C. After being stirred for 1 h, the resulting solution was allowed to warm to room temperature. After another 1 h, the solution was washed with brine and water and dried over $MgSO_4$, 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 1.6 g of yellow solid (70%): mp 119 °C; ^{1}H NMR ($CDCl_3$) δ 8.47−8.43 (m, 2H), 8.30 (q, 1H), 8.08 (s, 1H), 7.75 (s, 1H), 7.48−7.7.38 (m, 3H), 6.38 (q, 1H), 6.10 (q, 1H), 5.82 (q, 1H), 4.26 (t, 2H), 4.14 (t, 2H), 2.00−1.95 (m, 2H) 1.70−1.53 (m, 2H) 1.45−1.43 (m, 4H); IR (KBr pellet, cm^{-1}); 1724 ($\nu_{C=O\ of\ ester}$), 1590 and 1340 (ν_{nitro}).

Polymerization. 1.0 g (2.31 mmol) of **M1**, 0.89 g (6.92 mmol) of butyl acrylate, and 0.0753 g (0.461 mmol) of AIBN were dissolved in 10 mL of NMP. The solution was degassed by standard vacuum-freeze−thaw technique. After sealing the degassed ampule, 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 cold methanol to precipitate the polymer **P1**, which was purified by silicagel column chromatography (dichloromethane and THF) (1.3 g, 69%).

Photorefractivity Measurement. The photorefractive property of a 100 μm thick film of low T_g polymer **P1** was determined by two-beam coupling and degenerated four-wave mixing experiments. 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 633 nm He−Ne laser beams with equal powers of 60.7 mW/cm^2 were incident upon the sample. 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 an intensity

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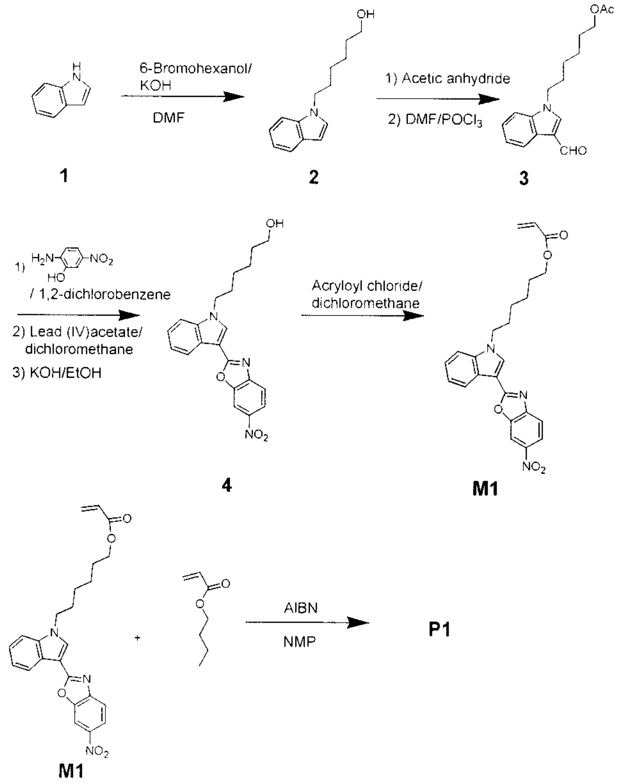
Scheme 1. Synthetic Pathway of Photorefractive Monomer (M1) and Polymer (P1)



of 1.27 mW/cm^2 counterpropagated to one of the writing beams as a reading beam.

Results and Discussion

In our previous work, we have reported the synthesis and properties of potentially photorefractive indole–benzoxazole-based polymethacrylate and polyacrylate.[8] These multifunctional polymers showed excellent electrooptic (EO) property and photoconductivity as expected from their structures. It was, however, difficult to fabricate 100 μm thick poled films from these high T_g polymers, which is required for photorefractive experiments partly due to their brittleness. To overcome this limitation and to impart orientational enhancement, low T_g photorefractive polyacrylate containing indole–benzoxazole-based monolithic chromophore was prepared in this work. The multifunctional chromophore (**4**), bearing long hexyl chain as spacer, was synthesized and incorporated into the side chain of polyacrylate. Butyl acrylate instead of the more common methyl methacrylate was used as a comonomer to effectively lower the T_g of polymer.[9] Polymer **P1** exhibited T_g of 15.1 °C below room temperature. The molecular weight of **P1**, determined by gel permeation chromatography, was $M_n = 7900$ and the polydispersity index was 4.98.

The inset of Figure 1 shows the UV–visible spectrum of **P1** in dichloromethane. The λ_{max} and $\lambda_{cut-off}$ were 370 and 480 nm which are ca. 100 nm blue-shifted compared to those of conventional NLO chromophores, DANS or DR1. To investigate the effect of TNF concentration, we prepared three samples of **P1** with the different amount of TNF (0, 0.2, and 1 wt %). Figure 1 shows the absorption coefficients of these samples in the visible region. It is seen that the absorption coefficients (α) at 633 nm were found to be 6.7, 7.0, and 12.4 cm^{-1}, for **P1** samples with 0, 0.2, and 1 wt % TNF, respectively.

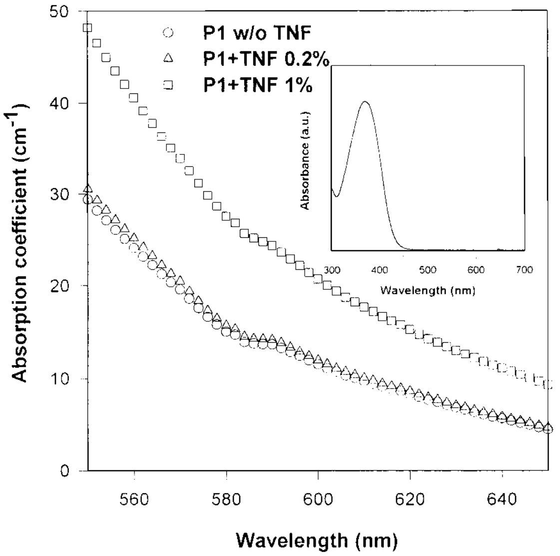


Figure 1. Absorption coefficients of **P1**/TNF (100/0, 99.8/0.2 and 99/1). The inset shows the UV–visible absorption spectrum of polymer **P1** in dichloromethane.

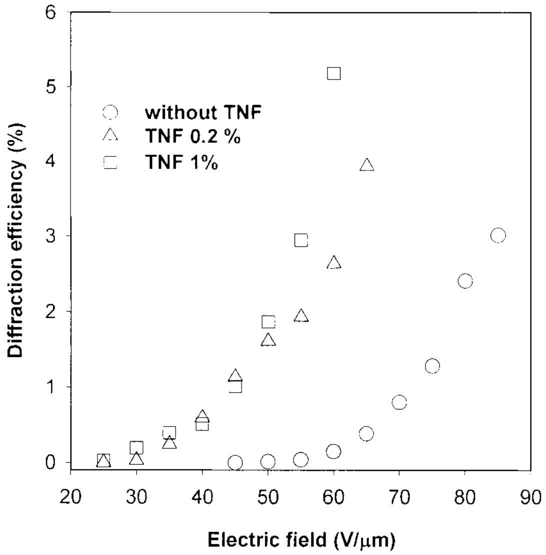


Figure 2. Electric field dependency of the steady-state diffraction efficiency.

Through the four-wave mixing experiment, diffraction efficiency was determined. Figure 2 presents the electric field dependencies of the steady-state diffraction efficiency. At the applied electric field of 60 V/μm, the diffraction efficiency for **P1** without TNF or doped with TNF (0.2 and 1 wt %) reached 0.15, 2.63, and 5.18%, respectively.

The unique characteristics of photorefractive effect is the nonlocal nature of the grating, which gives rise to the shift of the phase between the light intensity and the refractive index grating. The asymmetric energy transfer originating from this phase-shift can be investigated by two-beam coupling measurement. The obtained gain coefficients are shown in Figure 3. Most important result in this figure is that we obtained a photorefractive net-gain (3 cm^{-1}) with single component **P1** at the low electric field of 50 V/μm. This completes our argument that 3-(6-nitrobenzoxazol-2-yl)indole is a monolithic photorefracitive chromophore. We, of course, observed the increase of two-beam coupling gain with increasing TNF content as shown in Figure 3. However,

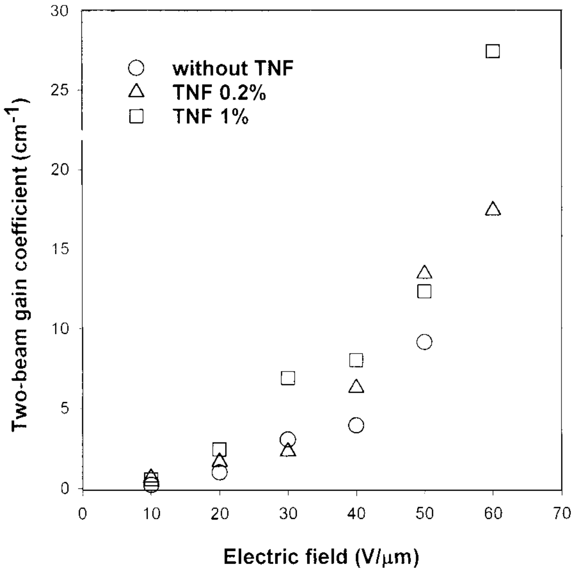


Figure 3. Effect of electric field on the photorefractive two-beam coupling gain.

the increase of gain was not similar to that of the diffraction efficiency, which was ascribed to the fact that TNF content affects not only the buildup of space charge field but also the trap density and subsequently, the phase shift. The two-beam coupling gain coefficient (Γ) of **P1**/ TNF (99/1 wt %) was 27.4 cm^{-1}, and its net-gain ($\Gamma-\alpha$) was 15.0 cm^{-1} at electric field of 60 V/μm.

Previously, we have reported the photorefractivity of polyacrylate containing indole-stilbene-based chromophore (**P2**).[8] This chromophore is structurally similar to that of **P1** except the stilbene-type linking group replacing benzoxazole moiety of **P1**. In contrast to the large photorefractivity of **P1**, **P2** with TNF (1 wt %) showed very low photorefractivity. Two-beam coupling gain coefficient of **P2**/TNF was 2.2 cm^{-1} at 75 V/μm and diffraction efficiency was 0.44% at 60 V/μm.

According to the EO measurement,[10,11] the NLO properties of **P1** and **P2** were comparable; the r_{33} value of **P1** was 4.27 pm/V and that of **P2** was 4.91 pm/V at 45 V/μm. Therefore, the significant enhancement in the photorefractivity of **P1** over **P2** seems to originate from the better efficiency of space-charge field formation. It is speculated that the wholly heteroaromatic benzoxazole linkage provided better photocharge generation and transport than stilbene-type one.

Conclusion

Low T_g (~15.1 °C) photorefractive polymer **P1** with a monolithic chromophore, 6-[3-(6-nitrobenzoxazol-2-yl)-indol-1-yl]hexan-1-ol (**4**) as a side chain, was synthesized and characterized. Photorefractive net gain of 3 cm^{-1} was obtained with a single-component **P1** film, which proved the monolithic photorefractivity of the indole–benzoxazole-type chromophore. The photorefractivity of **P1** was significantly enhanced by doping a small of sensitizer.

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