

Synthesis and Characterization of Carbazole-based Side-Chain Polymers for Photorefractivity

Dong Wook Kim, Soo Young Park, Sung Il Hong

*Department of Fiber and Polymer Science, Seoul National University, San 56-1,
Shinlim-dong, Kwanak-ku, Seoul 151-742, Korea*

Introduction

Photorefractive materials are of particular importance because they exhibit a reversible refractive index change under a low-power laser-beam illumination.¹ They can therefore be used as versatile storage media for erasable read-write optical memories or as reconfigurable interconnects.² Since the first report of photorefractivity in a polymer composite in 1991,³ a number of polymeric materials which exhibit the photorefractive effect have been prepared and characterized. To be photorefractive, a polymer needs to have second-order nonlinear optical (NLO) properties in addition to photoconductivity.² Among various photorefractive polymeric systems, fully functionalized polymers which have both the NLO chromophore and the charge transporting molecule attached to the polymer backbone are currently considered to be the most promising due to high chromophore content, improved temporal stability, and easy structural modification. In this work, we prepared carbazole-based fully functionalized polymers having NLO property and photoconductivity to be likely to satisfy the requirement for photorefractivity.

Experimental

Synthesis of monomers

6-Carbazol-9-yl-hexan-1-ol (1)

Powdered potassium hydroxide (44 g) was stirred with DMF(200 mL) at room temperature for 10 min. 9H-carbazole (26 g, 0.155 mol) was added slowly and stirred for 1 h. 6-

Chlorohexanol (23 ml, 0.172 mol) was added dropwise and the mixture was stirred at room temperature for 4 h and then at 40 °C for 12 h. The resulting mixture was poured into ice water and the precipitate was filtered, washed with water. The white solid was dissolved in chloroform and the insoluble residue was filtered out. The filtered chloroform solution was evaporated to remove solvent and the residue was purified by recrystallization from ethanol to give needle-like crystals (yield: 69%). mp 119~120 °C. IR (KBr pellet, cm^{-1}); 3302 ($\nu_{\text{O-H}}$), 2926-2858 ($\nu_{\text{aliphatic C-H}}$). $^1\text{H NMR}$ (CDCl_3); δ (ppm) = 8.0 (d, 2H), 7.4 (d, 2H), 7.3 (t, 2H), 7.1 (t, 2H), 4.2 (t, 2H, OCH_2), 3.5 (t, 2H, NCH_2), 1.8-1.3 (m, 8H, $(\text{CH}_2)_4$).

Acetic acid 6-carbazol-9-yl-hexyl ester (2)

A solution of 27 g of compound **1** in 200 mL of acetic anhydride was stirred and heated to reflux for 1 h. After cooling, the solution was poured into ice water and extracted with chloroform. The extract was dried over MgSO_4 and the solvent was removed at reduced pressure. IR (KBr window, cm^{-1}); 1740 ($\nu_{\text{C=O}}$). $^1\text{H NMR}$ (CDCl_3); δ (ppm) = 8.0 (d, 2H), 7.4 (d, 2H), 7.3 (t, 2H), 7.1 (t, 2H), 4.2 (t, 2H, OCH_2), 3.9 (t, 2H, NCH_2), 1.9 (s, 3H, COCH_3), 1.8-1.3 (m, 8H, $(\text{CH}_2)_4$).

Acetic acid 6-(3-formyl-carbazol-9-yl)-hexyl ester (3)

32.9 g (0.106 mol) of compound **2** was dissolved in DMF (100 mL) and phosphorus oxychloride (19.76 ml) was added dropwise to the solution at 0 °C. The brown solution was stirred for 30 min and heated at 100 °C for 2 h. After cooling, the dark brown solution was poured into ice water and neutralized to pH 6-8 with sodium hydroxide 2 N solution. The mixture was extracted with chloroform and the extract was dried over MgSO_4 . The solvent was removed at reduced pressure and the residue was purified by silica gel column chromatography (ethyl acetate / chloroform = 1/2) to give light yellow colored solid (yield: 73%). mp 51~52 °C. IR (KBr pellet, cm^{-1}); 2822 and 2735 ($\nu_{\text{C-H}}$ of aldehyde), 1684 ($\nu_{\text{C=O}}$ of aldehyde). $^1\text{H NMR}$ (CDCl_3); δ (ppm) = 10.1 (s, 1H, aldehyde proton), 8.6 (s, 1H), 8.2 (d, 1H), 8.0 (d, 1H), 7.6-7.5 (m, 3H), 7.3 (t, 1H), 4.4 (t, 2H, OCH_2), 4.0 (t, 2H, NCH_2), 2.0 (s, 3H, COCH_3), 1.9-1.4 (m, 8H, $(\text{CH}_2)_4$).

9-(6-Hydroxy-hexyl)-9H-carbazol-3-carbaldehyde (4)

26.1 g of compound **3** was dissolved in ethanol / water mixture and 10.0 g of potassium hydroxide was added into the solution. The resulting solution was heated to reflux for 3 h. After cooling, about half the solvent was removed at reduced pressure and the residue was poured into water. The precipitate was filtered and washed thoroughly with water. After drying under vacuum, the solid was recrystallized from ethanol to give yellow colored solid. mp 72~74 °C. IR (KBr pellet, cm^{-1}); 3410 ($\nu_{\text{O-H}}$), 2741 ($\nu_{\text{C-H}}$ of aldehyde), 1684 ($\nu_{\text{C=O}}$ of aldehyde). $^1\text{H NMR}$ (DMSO-

d₆); δ (ppm) = 10.0 (s, 1H, aldehyde proton), 8.7 (s, 1H), 8.3 (d, 1H), 8.0 (d, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 7.5 (t, 1H), 7.3 (t, 1H), 4.5 (t, 2H, OCH₂), 4.3 (t, 1H, OH), 3.3 (t, 2H, NCH₂). 1.8-1.3 (m, 8H, (CH₂)₄).

2-Methyl-acrylic acid 6-(3-formyl-carbazol-9-yl)-hexyl ester (5).

5.91 g (0.02 mol) of compound **4** was dissolved in freshly distilled tetrahydrofuran (THF) (40 mL). Pyridine (1.61 mL) and a trace amount of 2,6-di-*tert*-butyl-4-methyl phenol (polymerization inhibitor) were added to the solution. The solution was cooled in ice bath and 1.95 mL (0.02 mol) of methacryloyl chloride was added slowly under nitrogen atmosphere. After stirring at 0 °C for 30 min, the solution was heated at 40 °C for 24 h. The resulting solution was poured into sodium bicarbonate solution and then washed with water. The mixture was extracted with ethyl acetate and dried over MgSO₄. The solvent was removed at reduced pressure and the residue was purified by silica gel column chromatography (n-hexane / ethyl acetate = 3/1) to give viscous oil. IR (KBr window, cm⁻¹); 2816 and 2735 (ν_{C-H} of aldehyde), 1714 ($\nu_{C=O}$ of ester), 1686 ($\nu_{C=O}$ of aldehyde). ¹H NMR (CDCl₃); δ (ppm) = 9.9 (s, 1H, aldehyde proton), 8.4 (s, 1H), 7.9 (d, 1H), 7.6 (d, 1H), 7.3-7.1 (m, 4H), 5.8 and 5.3 (2H, vinyl protons), 4.1 (t, 2H, OCH₂), 3.9 (t, 2H, NCH₂), 1.9 (s, 3H, CH₃), 1.7-1.2 (m, 8H, (CH₂)₄).

2-methyl-acrylic acid 6-[3-[2-cyano-2-(4-nitrophenyl)-vinyl]-carbazol-9-yl]hexyl ester (CNM)

To a stirred solution of compound **5** (2.0 g, 5.5 mmol) in THF was added 4-nitrophenyl acetonitrile (0.97 g, 6.0 mmol) and a trace amount of 2,6-di-*tert*-butyl-4-methyl phenol. When the mixture was dissolved, piperidine (2.18 mL) was added, and the solution allowed to stir at 40 °C for 24 h. The resultant solution was then cooled to room temperature and precipitated into ethanol. The precipitate filtered was dissolved in THF and then poured into ethanol / water mixture. The red solid was filtered and then dried under vacuum. (yield : 58 %). mp 171~173 °C. IR (KBr pellet, cm⁻¹); 2208 (ν_{CN}), 1716 ($\nu_{C=O}$), 1678 ($\nu_{C=C}$ of vinyl group), 1516 and 1338 (ν_{nitro} group). ¹H NMR (CDCl₃); δ 8.6-7.2 (m, 12H), 6.0 (s, 1H), 5.4 (s, 1H), 4.3 (t, 2H, OCH₂), 4.0 (t, 2H, NCH₂), 1.8 (s, 3H, CH₃), 1.6-1.4 (m, 8H, (CH₂)₄).

Synthesis of polymers

Monomer CNM, comonomer MMA, and AIBN (5 mol% to the total monomers) as an initiator were dissolved in THF. The solution was thoroughly degassed by several freeze-pump-thaw cycles and heated in a sealed ampoule at 65 °C for 2 days. The resulting solution was cooled

and poured into vigorously agitated ethanol to precipitate solid. In order to purify the product, several reprecipitations from THF to ethanol were performed.

Results and discussion

Polymer preparation and characterization

Side-chain polymers were prepared by a radical polymerization reaction of monomer CNM and comonomer MMA. Characterization and physical properties of polymers are summarized in Table 1.

Table 1. Characterization of polymers.

Polymer	Conversion (%)	Composition ^a CNM / MMA	Mw ^b	Mw / Mn ^b	T _g (°C)
CNMMP	75	1 / 1	22,700	1.87	118
CNMM3P	77	1 / 3	19,800	1.66	102

^a calculated by ¹H NMR spectroscopy

^b determined by GPC with polystyrene standard in THF eluent

NLO properties of polymers

Thin polymer films were spin-coated on slide glass or indium-tin oxide (ITO) coated glass. Residual solvent was removed by heating the films in vacuum oven for several days. For electrooptic coefficient measurement, contact poling of polymer film was carried out. The electrooptic coefficient (r_{33}) of poled polymer CNMM3P measured at the wavelength of 632.8 nm (He-Ne laser) using a simple reflection method proposed by Teng et al.⁴ was found to be 3.68 pm/V. SHG coefficient (d_{33}) of CNMMP and CNMM3P determined by the Marker-fringe method at 1.064 μ m fundamental wavelength was as large as 23.26 pm/V and 17.07 pm/V, respectively.

Photoconductivity measurement

The dark and photoconductivity of polymer CNMMP film were measured under room temperature using a Keithley 617 electrometer and a Oriel 200-500 W Xe/Hg lamp was used as a UV-visible light source. Figure 1 shows the I-V characteristics for CNMMP in dark and photostate.

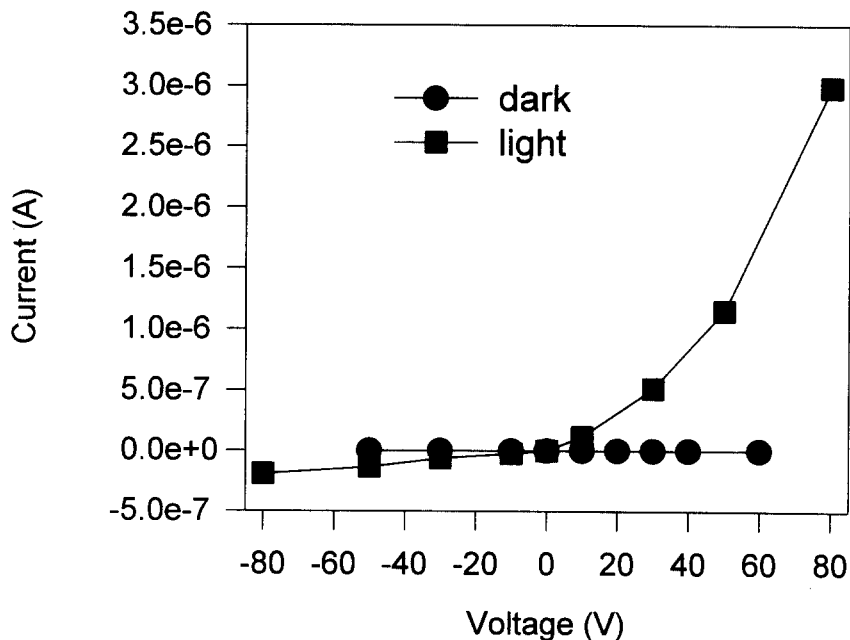


Figure 1. I-V curve of polymer CNMMP film.

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References

1. D. D. Nolte, *Photorefractive effects and Materials*, Kluwer Academic Publishers, 1995.
2. W. E. Moerner and S. M. Silence, *Chem. Rev.* **94** (1), 127 (1994).
3. S. Ducharme, J. C. Scotte, R. J. Twieg, and W. E. Moerner, *Phys. Rev. Lett.* **66**, 1846 (1991).
4. Teng, C. C.; Meñ, H. T. *Appl. Phys. Lett.* **1990**, 56, 1754.