Polymer Bulletin 42, 175–181 (1999)

Polymer Bulletin

Synthesis and properties of nonlinear optical chromophores and polymers containing 6-nitroquinoline as π-electron acceptor

Yong Ha Hwang, Jong Lae Kim, Soo Young Park*, **Sung II Hong**

Department of Fiber and Polymer Science, Seoul National University, San 56-1,
Shillim-dong, Kwanak-gu, Seoul 151-742, Korea

Received: 29 September 1998/Revised version: 7 December 1998/Accepted: 11 December 1998

Summary

Two nonlinear optical (NLO) methacrylate monomers, 2-methyl-acrylic acid 2-(ethyl-{4-[2-(6-nitro-quinolin-2-yl)-vinyl]-phenyl}-amino)-ethyl ester **(5)** and 2-methyl-acrylic acid 6-{3-[2-(6-nitro-quinolin-2-yl)-vinyl]-carbazol-9-yl}-hexyl ester **(7)** were newly synthesized and copolymerized with methylmethacrylate to give NLO polymers, **P1** and **P2**. These polymers were well soluble in organic solvents and showed glass transition temperatures at 145 °C and 114 °C, respectively. The number average molecular weights (Mn) were 26,600 for **P1** and 9,300 for **P2**. The SHG coefficients (d33) of corona-poled films of **P1** and **P2** measured with 1.064 μm Nd-YAG laser were 32.2 pm/V and 17.6 pm/V, respectively.

Introduction

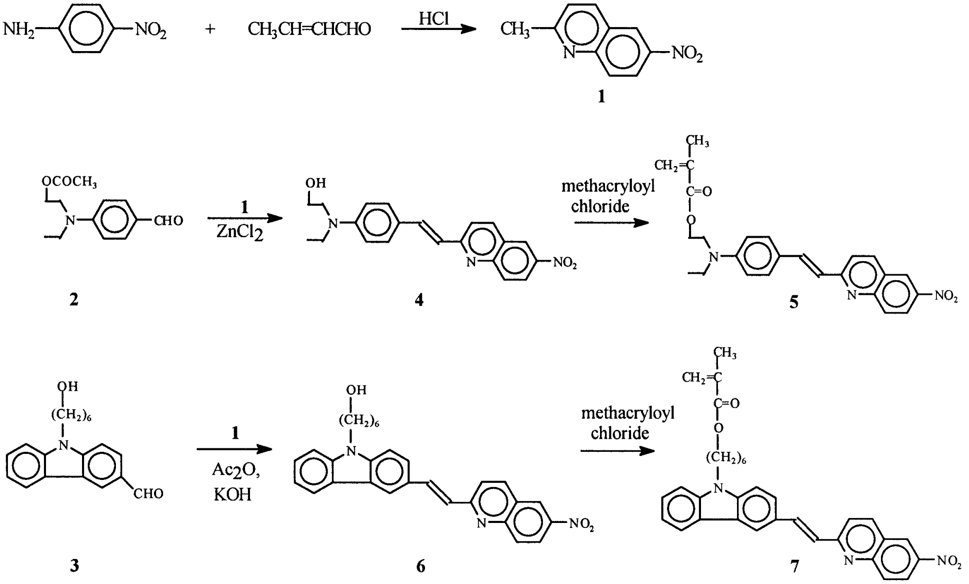
In order to be useful in practical device application, second-order nonlinear optical (NLO) polymers should possess not only the higher molecular hyperpolarizability of chromophores but also the better thermal and chemical stability to prevent the dipolar relaxation of noncentrosymmetric alignment (1,2). To this end, various NLO chromophores and polymers containing fused heteroaromatic donor units like 3-[2-cyano-2-(4-nitrophenyl)-vinyl]-carbazole and 3-[2-(4-nitrophenyl)-vinyl]-carbazole were investigated by us (3,4). It was found that the fused heteroaromatic carbazole structure as a π-electron donor imparted a stable NLO and photoconductive property to the chromophores and polymers. The observation of distinct photoconductivity as well as the stable NLO activity from a single chromophore suggested its potential use as a monolithic photorefractive polymer (4,5).

As an extension of this idea, we came to consider a fused heteroaromatic acceptor moiety of NLO chromophore. 6-Nitroquinoline seemed most adequate for this purpose, since the quinoline itself is a stable and electron-deficient fused heteroaromatic ring. The thermal and chemical stability and also the photoconducting property of quinoline-containing polymers were reported earlier by us (6,7).

In this work, two NLO chromophores containing 6-nitroquinoline as a π-electron acceptor were newly synthesized. One of them ([ethyl-{4-[2-(6-nitro-quinolin-2-yl)-vinyl]-phenyl}-amino]-ethanol (**4**)) contains substituted aniline, and the other (6-{3-[2-(6-nitro-quinolin-2-yl)-vinyl]-carbazol-9-yl}-hexan-1-ol (**6**)) contains carbazole as π-electron donor. These chromophores were reacted with methacryloyl chloride to give NLO methacrylate monomers **5** and **7**. Copolymerization of these monomers with methylmethacrylate yielded NLO polymers **P1** and **P2**. We report the details of the

---

* Corresponding author



Scheme 1. Synthesis of NLO chromophores and monomers.

synthesis, optical property, and the second-harmonic generation (SHG) from these 6-nitroquinoline-containing NLO polymers.

Experimental

As shown in Scheme 1, 6-nitroquinaldine **(1)** was prepared from *p*-nitroaniline and crotonaldehyde. Acetic acid 2-[ethyl-(4-formyl-phenyl)-amino]-ethyl ester **(2)** and 9-(6-hydroxy-hexyl)-9H-carbazol-3-carbaldehyde **(3)** were prepared according to the literature methods starting from 2-(N-ethylanilino)ethanol and carbazole, respectively (8,4). NLO chromophores **4** and **6** were prepared by the condensation reactions of **1** with **2** and **3**, respectively. Monomers (**5** and **7**) were obtained by the reactions of these chromophores (**4** and **6**) with methacryloyl chloride.

6-nitroquinaldine **(1)***:*

15 g (0.1086 mol) of *p*-nitroaniline was dissolved in 60 mL of concentrated HCl solution and heated under reflux. To this solution, 9.5 g (0.1355 mol) of crotonaldehyde was added dropwise over 1 h, and the mixture was further refluxed for 45 min. The reaction mixture was cooled to room temperature and poured into water. Then, a small amount of tar product was removed by filtration. Resulting solution was neutralized by 10% sodium hydroxide solution to precipitate the solid product. After filtration, the crude product was collected and recrystallized from methanol. 9.66 g (47 %) of yellow solid was obtained, mp 165 °C. FT-IR (KBr pellet, cm^{-1}); 1518 and 1342 ($\nu_{N\text{-}O}$ of NO_2). ^1H NMR ($CDCl_3$); δ 2.82 (s, 3H, methyl protons), δ 7.44~8.76 (m, 5H, aromatic protons). Anal. Calcd for $C_{10}H_9N_2O_2$: C, 63.8; H, 4.28; N, 14.9. Found: C, 62.5; H, 3.98; N, 15.2.

[ethyl-4-[2-(6-nitro-quinolin-2-yl)-vinyl]-phenyl}-amino]-ethanol **(4)***:*

The mixture of 6-nitroquinaldine (**1**) (1.88 g, 0.01 mol), acetic acid 2-[ethyl-4-formyl-phenyl]-amino]-ethyl ester (**2**) (2.35 g, 0.01 mol), and 0.1 g of $ZnCl_2$ was charged into a

100 mL round bottom flask and heated to 165 °C for 2 h. Then the mixture was cooled to room temperature. Addition of small amount of aqueous HCl solution into the mixture resulted in the dissolution of the crude product. The acidic solution was neutralized by ammonium hydroxide and the solid was precipitated. Product was washed with water and 0.76 g (21 %) of pure product was recrystallized from methanol, mp 168-169 °C. FT-IR (NaCl window, cm^{-1}); 3381 ($\nu_{O\text{-}H}$ of hydroxyl), 1520 and 1330 ($\nu_{N\text{-}O}$ of NO_2). ^1H NMR ($CDCl_3$); δ 8.69~6.76 (m, 11H, aromatic protons including CH=CH), 1.60 (s, 1H, OH), 3.46 (q, 2H, NCH_2), 3.85 and 3.53 (t, 4H, NCH_2CH_2), 1.22 (t, 3H, CH_3). Anal. Calcd. for $C_{21}H_{19}N_3O_3$: C, 69.8;H, 5.3;N, 11.6. Found: C, 69.1; H, 5.5;N, 11.0.

2-methyl-acrylic acid 2-(ethyl-{4-[2-(6-nitro-quinolin-2-yl)-vinyl]-phenyl}-amino)-ethyl ester **(5)***:*

A mixture of [ethyl-{4-[2-(6-nitro-quinolin-2-yl)-vinyl]-phenyl}-amino]-ethanol **(4)** (0.74 g, 0.002 mol), triethylamine (1.39 mL, 0.10 mol), a trace of 2,6-di-*tert*-butyl-4-methylphenol (polymerization inhibitor) and 30 mL of chloroform was cooled to 0 °C and treated dropwise with a solution of 0.52 g (0.005 mol) of distilled methacryloyl chloride in 10 mL of chloroform under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h and then at 37 °C for 22 h. After cooling the reaction mixture, the resulting solution was washed with saturated aqueous sodium bicarbonate and then water. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, 0.52 g (60 %) of the product was separated on a silica gel column, using chloroform as eluent, mp 167-168 °C. FT-IR (NaCl window, cm^{-1}) 1718 ($\nu_{C=O}$ of ester), 1261 ($\nu_{C\text{-}O}$ of ester), 1524 and 1330 ($\nu_{N\text{-}O}$ of NO_2), 1600 ($\nu_{C=C}$ of aromatic). ^1H NMR ($CDCl_3$); δ 8.69~6.76 (m, 11H, aromatic protons including CH=CH), 6.23 and 5.58 (s, 2H, vinyl protons), 3.48 (q, 2H, NCH_2), 4.34 and 3.67 (t, 4H, NCH_2CH_2), 1.22 (t, 3H, CH_3), 1.95 (s, 3H, acrylic CH_3). Anal. Calcd. for $C_{25}H_{23}N_3O_4$: C, 69.9;H, 5.4;N, 9.8. Found: C, 69.2;H, 5.5;N, 9.6.

6-{3-[2-(6-nitro-quinolin-2-yl)-vinyl]-carbazol-9-yl}-hexan-1-ol **(6)***:*

6-nitroquinaldine **(1)** (3.3 g, 1 eq mol) and 9-(6-hydroxy-hexyl)-9H-carbazol-3-carbaldehyde **(3)** (15.58 g, 3 eq mol) were dissolved in a 16 g of acetic anhydride, and heated to 165 °C under reflux. After stirring for 4 h, the mixture was cooled to room temperature. Addition of a small amount of acetone into the mixture resulted in the precipitation of the orange-colored crude product. After washing three times with ethanol, it was dissolved in $CHCl_3$ and reprecipitated into ethyl acetate. To the 100 mL of ethanol solution of this product was added 10 g of potassium hydroxide. After refluxing for 2 h, the mixture was poured into water. 2.5g (31%) of yellow solid was precipitated, mp 140-141 °C. FT-IR (KBr pellet, cm^{-1}); 3367 ($\nu_{O\text{-}H}$ of hydroxyl), 3031 ($\nu_{C\text{-}H}$ of aromatic C-H), 2926 ($\nu_{C\text{-}H}$ of aliphatic C-H), 1529 and 1331 ($\nu_{N\text{-}O}$ of NO_2). ^1H NMR ($CDCl_3$); δ 8.75~7.28 (m, 14H, aromatic protons including CH=CH), 4.35 (t, 2H, OCH_2), 4.05 (t, 2H, NCH_2), 2.04 (s, 1H, OH), 1.50 ~ 1.45 (m, $(CH_2)_4$, 8H). Anal. Calcd. for $C_{29}H_{31}N_3O_4$: C, 74.8;H, 5.8;N, 9.0. Found: C, 73.6;H, 5.6;N, 9.8.

2-methyl-acrylic acid 6-{3-[2-(6-nitro-quinolin-2-yl)-vinyl]-carbazol-9-yl}-hexyl ester **(7)***:*

A mixture of 6-{3-[2-(6-nitro-quinolin-2-yl)-vinyl]-carbazol-9-yl}-hexan-1-ol **(6)** (2.30 g, 0.0049 mol), pyridine (1.87 ml), a trace of 2,6-di-*tert*-butyl-4-methylphenol and 100 mL of THF was cooled to 0 °C and treated dropwise with a solution of 2.5 g (0.025 mol) of distilled methacryloyl chloride in 5 mL of THF under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 2 h and then at 40 °C for 48 h. After cooling the reaction mixture, it was washed with saturated aqueous sodium bicarbonate to precipitate 1.8 g (69 %) of yellow product, mp 164-165 °C. FT-IR (KBr pellet, cm^{-1}); 1528 and 1335 ($\nu_{N\text{-}O}$ of NO_2), 1724 ($\nu_{C=O}$ of ester), 1259 ($\nu_{C\text{-}O}$ of ester). ^1H NMR ($CDCl_3$); δ 8.66~7.22 (m, 14H, aromatic protons including CH=CH), 6.00 and 5.47 (s, 2H, vinyl protons), 4.26 (t, 2H, OCH_2), 4.05 (t, 2H, NCH_2), 1.81 (s, 3H, acrylic protons), 1.61-1.37 (m, 8H, $(CH_2)_4$). Anal. Calcd. for $C_{33}H_{31}N_3O_4$: C, 74.3;H, 5.8;N, 7.8. Found: C, 73.1;H, 5.2;N, 8.2.

Polymerization:
A mixture of **5** (0.431 g, 0.001 mol), distilled MMA (0.32 mL, 0.003 mol), AIBN (0.0066 g, 1 mol %) and 7.5 ml of dried $CHCl_3$ was degassed by standard freeze/thaw technique and heated in a sealed ampoule in *vacuo* at 60 °C for 72 h. The resulting solution was poured into 200 mL of methanol to precipitate the polymer (**P1**). The polymer was purified by reprecipitation from $CHCl_3$ into methanol and dried in *vacuo* at 55 °C. Polymer **P2** was similarly prepared by the copolymerization of 7 with MMA.

Characterization:
IR spectra were taken by transmission on a MIDAC M FT-IR spectrometer. ^1H NMR spectra were recorded with a BRUKER AMX 300 spectrometer. Elemental analyses were carried out with a Carlo Erba 116 Elemental Analyzer with a LECO CHNS 932. Differential scanning calorimetry (DSC) measurements were performed on a PERKIN-ELMER DSC 7 under heating rates of 10°C/min. The molecular weights and polydispersity were determined with a Waters HPLC component system calibrated with polystyrene standard. UV-visible spectra were measured on Shimadzu UV-2101 PC Spectrophotometer.

Film preparation:
NLO polymers **P1** and **P2** were dissolved in monochlorobenzene and the solutions (13 wt %) were filtered through a Teflon membrane filter (0.2 μm pore). Thin polymer films were spin coated from these solutions and dried in vacuo.

Poling:
Films of **P1** and **P2** were subjected to corona poling at 145 °C and 123 °C, respectively. 5 kV dc was applied to the corona wire placed 10 mm above the film surface. After 15 min, the film was rapidly cooled down to room temperature with the voltage kept on.

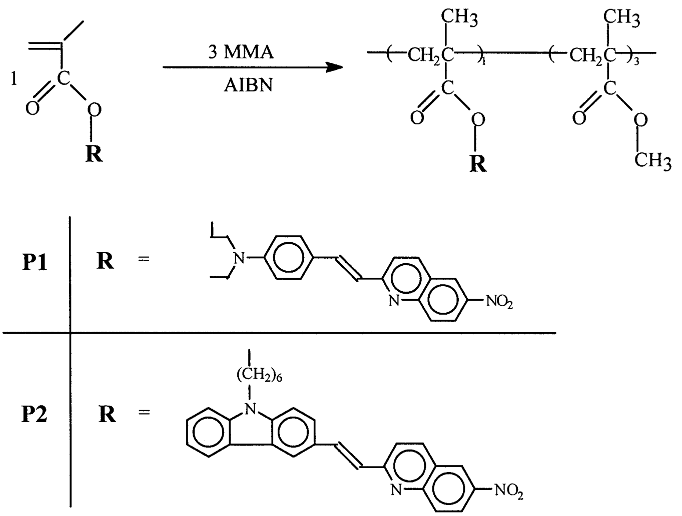
SHG measurement :
The second harmonic generation (SHG) properties of poled **P1** and **P2** films were measured by means of the Maker fringe method. SHG signal was monitored at incident angle (θ) of -80° ~ +80° using Nd-YAG 1064 nm laser as a fundamental beam. The frequency-doubled output (532 nm) from the sample was separated using interference filters and detected by a photomultiplier and a gated integrator interfaced with a computer. Maker fringes were analyzed by fitting theoretical functions with reference to that of y-cut quartz, which yielded the SHG coefficients, d_{33} and d_{31} (9).

Results and Discussion

Synthesis and Characterization:

6-nitroquinaldine **(1)** was successfully synthesized by the Skraup reaction of *p*-nitroaniline and crotonaldehyde in 47% yield. As a donor part of NLO chromophore, acetic acid 2-[ethyl-(4-formyl-phenyl)-amino]-ethyl ester(**2**) was prepared in three steps according to the literature method (8). Carbazole-containing donor part, i.e. 9-(6-hydroxy-hexyl)-9H-carbazol-3-carbaldehyde was synthesized in four steps from carbazole as reported earlier by us (4). NLO chromophores (**4**,**6**) bearing 6-nitroquinoline as an acceptor could be synthesized by the alkene forming condensation reactions of 6-nitroquinaldine (**1**) with the donor part compounds (**2**,**3**) in the presence of acetic anhydride or zinc chloride. The yields of these reactions were quite low (21%, 31%) presumably due to the unoptimized reaction codition and work-up procedure. Additional hydrolysis step was required in the synthesis of **6**, because it was prepared as an acetate ester by reaction with acetic anhydride. The methacrylate monomers (**5**,**7**) were synthesized by the esterification reaction of methacryloyl chloride with **4** or **6** in 60% and 69% yields, respectively.

Initial attempts to homopolymerize the monomer **5** or **7** by radical means failed presumably because the nitro group in NLO chromophore functioned as a chain transfer site. However, these monomers could be copolymerized with MMA by free radical initiation to give the high molecular weight polymers as depicted in Scheme 2. The polymerization solvents were chloroform for **P1** and THF for **P2**, respectively. Table 1 shows the conversion, molecular weight, polydispersity, and the glass transition temperature (Tg) of these polymers. Polymers **P1** and **P2** were very well soluble in common organic solvents like tetrachloroethane or chlorobenzene. Thin polymer films of high optical quality and smooth surface could be prepared by spin coating of these polymer solution.



Scheme 2. Polymerization.

Table 1. Synthesis and properties of NLO polymers

polymer	conversion (%)	Mn[a]	Mw/Mn[a]	T_g[b]
P1	74	26,600	2.07	145
P2	64	9,300	1.72	114

[a] *Values were obtained by GPC analysis with polystyrene standard*
[b] *Determined by differential scanning calorimetry*

The molar ratio of the NLO monomer (**5** or **7**) to MMA, *i.e.* the composition of the monomer mixture was 1:3. Chemical structures of **P1** and **P2** were fully identified by ^{1}H NMR and FT-IR. It was found by the integration of ^{1}H NMR signals of polymer that the composition of copolymer was close to that of monomer mixture. Glass transition temperatures of **P1** and **P2** were determined by DSC to be 145 °C and 114 °C. Lower Tg value of **P2** compared to **P1** is attributed to the longer spacer length of the former (hexylene in **P2**, ethylene in **P1**). However, it was noted that this Tg value of **P2** is 12 °C higher than that of otherwise same copolymer which contains 4-nitrobenzene as an acceptor part (4). It is considered that the bulkier quinoline unit is responsible to the increase of Tg.

Nonlinear optical properties:

Due to the intramolecular charge transfer states, **P1** and **P2** showed electronic absorption in the visible region. Absorption maxima (λ_{max}) of **P1** was at 452 nm and that of **P2** was at 424 nm. This difference of λ_{max} is related to the donor strength of NLO chromophore because the remaining structures are same for both chromophores. It is clear that the donor strength of **P1**(aniline derivative) is stronger than that of **P2** (carbazole derivative).

The noncentrosymmetric alignment of chromophores, which is essential for the second order nonlinear optical effect, was achieved by corona poling. Fig. 1 compares the UV-visible absorption spectra of **P1** before and after poling. After poling, the absorbance of film decreased significantly due to the dipolar alignment of the chromophore. The order parameters ($\Phi = 1 - A2/A1$) of poled **P1** and **P2** films were calculated to be 0.12 and 0.23 respectively, where A1 and A2 are the absorbances before and after poling. As shown in Figure 1(c), relaxation at 145 °C without electric field resulted in the recovery of absorbance. This demonstrates that the reduction of absorbance by poling is not due to the thermal decomposition but is due to the orientation of the chromophore. The poling conditions and the achieved order parameters are summarized in Table 2.

Table 2. Poling condition and order parameter of polymer film

Polymer	Poling condition	λ_{max} (nm)	Order parameter (Φ)
P1	145 ℃, 5 kV, 15 min.	452	0.12
P2	123 ℃, 5 kV, 15 min	424	0.23

Table 3. Film thickness and SHG coefficients

Polymer	Film thickness (μm)	d_{31} (pm/V)	d_{33} (pm/V)
P1	0.42	12.1	32.2
P2	0.45	6.5	17.6

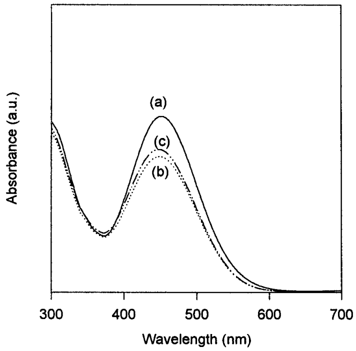


Fig. 1. UV-visible spectra of P1; (a) before poling, (b) after poling (145 °C, 5 kV, 15 min), and (c) after relaxation (145 °C, 15 min).

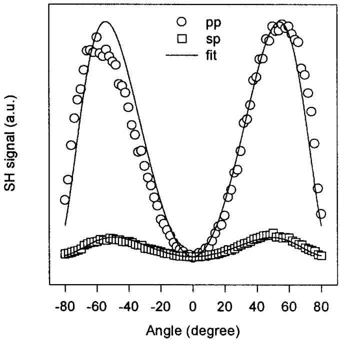


Fig. 2. Maker fringe of P1 showing SHG intensity as a function of incident angle.

The Maker fringe pattern of **P1** is shown in Fig. 2 and the calculated SHG coefficients of the polymers are listed in Table 3. Large values of SHG coefficients were observed even though the order parameters(ϕ) were as low as 0.12 and 0.23. Because the SHG coefficients are to increase with ϕ, much higher optical nonlinearity is expected after the optimization of poling conditions. As a final remark, the seemingly higher d_{33} and d_{31} values of **P1** than those of **P2** are partly attributed to the higher resonance enhancement, since the former absorbs at the longer wavelength.

Conclusion

Novel nonlinear optical chromophores and polymers containing 6-nitroquinoline as an electron acceptor part were successfully synthesized and characterized.

Acknowledgment

YHH acknowledges Dr. D. W. Kim and Mr. H. S. Moon for the invaluable advice and SHG measurement.

References

1. Miller RD, Burland DM, Jurich M, Lee VY, Moylan CR (1995) Macromolecules 28:4970
2. Trollsas M, Sahlen F, Gedde UW, Hult A(1995) Macromecules 29:2590
3. Kim DW, Hong SI, Park SY, Kim N (1997) Bull. Kor. Chem. Soc. 18:198
4. Kim DW, Moon HS, Park SY, Hong SI (1998) React. & Funct. Polym. *in press*
5. Zhang Y, Wada T, Wang L, Aoyama T, Sasabe H (1996) Chem. Commun. 2325
6. Kim KA, Park SY, Kim YJ, Kim N, Hong SI, Sasabe H (1992) J. Appl. Polym. Sci. 46:1
7 Choi D, Lee EJ, Kim KA, Park SY, Kim N (1993) J. Appl. Polym. Sci. 50:1429
8. Robello DR (1990) J. Polym. Sci; Pt A Polym. Chem. 28:1
9. Jerphagnon J, Kurtz, SK (1970) J. Appl. Phys. 41:1667