

## Synthesis and Characterization of Nonlinear Optical Polymers Having Quinoline-based Chromophores

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We synthesized three kinds of chromophores incorporating aromatic quinoline unit as a  $\pi$ -conjugated bridge in order to prepare more thermally stable nonlinear optical (NLO) chromophores than general stilbene unit. The NLO poly(methylmethacrylate) copolymer, polyimides, and polyester were successfully synthesized by these corresponding quinoline-based monomers. Their physical and optical properties were investigated by thermogravimetry, gel permeation chromatography, ultraviolet-visible spectroscopy, second harmonic generation (SHG) and electro-optic (EO) measurement. All the polymers exhibited better thermal stability, however their NLO activity was a little lower than that of general stilbene-based NLO polymers. Among three kinds of polymers, the PMMA copolymer with quinoline chromophores had the largest SHG coefficient  $d_{33}$  value of 27 pm/V (at 1.064  $\mu\text{m}$ ) and EO coefficient  $r_{33}$  value of 6.8 pm/V (at 1.3  $\mu\text{m}$ ).

**Keywords :** Quinoline chromophores, Electro-optic polymers, Nonlinear optical polymers.

### Introduction

The signal propagation and switching using electron as a carrier should be changed to new system using photon in order to process enormous data faster in computing and telecommunications technology. One of the important components in optical communication system would be an optical switch to digitalize all information signals. A conventional optical switching material is an inorganic crystal, for example lithium niobate. Many organic chemists have attempted to substitute the expensive inorganic crystals with low-cost organic materials, for example, side-chain nonlinear optical (NLO) polymers.<sup>1</sup> The advantages of NLO polymers compared to inorganic crystals include the easier fabrication of optical waveguides on device substrate, lower dielectric constants, and potentially higher NLO susceptibility, etc.<sup>2</sup> Many researches have been focused on the enhancement of NLO activity and improvement of its temporal stability during prolonged period. For higher NLO activity, a variety of NLO chromophores have been designed and synthesized by changing the strength of electron donors and electron acceptors, and the type of  $\pi$ -conjugated bridge or its length in chemical structure of chromophore, respectively.<sup>3-5</sup> Alike to inorganic crystals, the NLO moieties (*e.g.* donor-bridge-acceptor) attached in polymer backbones must be oriented one directionally by external electric field, but after removing the field the residual orientation tends to be randomized after long period or at high temperature. Therefore, it is the most important to maintain the one directional alignment of NLO chromophores in polymer matrix for a long period. For this, the high glass temperature ( $T_g$ ) polymers such as polyimide

or polyquinoline have been proposed for a NLO polymer backbones.<sup>6,7</sup> Some results reveal that high  $T_g$  polymers can be good candidate materials for long-life NLO application, even if their NLO coefficients should be increased for actual application. For adopting high  $T_g$  polymers, thermally stable NLO chromophore even at high poling temperature began to be necessary.<sup>8</sup>

In our earlier study, we have introduced an aromatic benzoxazole unit as a new  $\pi$ -conjugated bridge in a chromophore structure for better thermal and photochemical stabilities, and demonstrated the difference of thermal and temporal stabilities of benzoxazole from that of stilbene-based NLO chromophores bearing poly(methylmethacrylate) (PMMA) copolymers<sup>9</sup> and the other polymer system.<sup>10-13</sup>

In this study, we newly synthesized three kinds of quinoline-based NLO chromophores instead of benzoxazole, and three kinds of NLO polymers (PMMA, polyester, and polyimide) therefrom. We report here in detail the synthesis and characterization of new quinoline-based NLO polymers. In addition, their thermal properties, second harmonic generation and electro-optic properties of the polymers were investigated.

### Experimental Section

**Materials.** 1-Fluoro-4'-nitrobenzene, 4-fluoroacetophenone, 4-nitrocinnamaldehyde, tetrachloro-1,4-benzoquinone (*p*-chloroanil), 2-amino-5-nitro-benzophenone, diisopropyl azodicarboxylate (DIAD), triphenylphosphine (TPP), 2-(methylamino)ethanol, diethanolamine, cesium fluoride, potassium carbonate, 10% palladium on carbon, 18-crown-6 were purchased from Aldrich Co. Tetrahydrofuran (THF), dimethylsulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), methacryloyl chloride, and methyl methacrylate (MMA) were

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used after distillation. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use.

**Synthesis of 2-(methyl-4-nitroanilino)-1-ethanol (1).** Into a 250 mL flask added 20 g (142 mmol) of 1-fluoro-4-nitrobenzene and 19.6 g (142 mmol) of potassium carbonate and 20 mL of DMSO. This mixture was heated to 95 °C with stirring. The solution of 15.9 g (213 mmol) of 2-(methyl-amino)ethanol in 10 mL of DMSO was added slowly into the reactant and followed by adding 0.1 g of 18-crown-6. The mixture was stirred at this temperature for 24 h. The reactants were poured into cold water to precipitate the product. The product was purified by recrystallization from ethanol, giving yellow crystals (yield: 24 g, 86%).

mp 105 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.04 (s, 3H, NCH<sub>3</sub>), 3.52 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.67 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 4.79 (t, 1H, OH), 6.82 (d, 2H, ArH), and 7.98 ppm (d, 2H, Ar-H).

**Synthesis of 2-methyl-[2-(4-nitrophenyl)-6-quinoly]amino-1-ethanol (3, Qn1).** Into a 250 mL flask, added the portion of 5.91 g (0.03 mol) of **1** and 0.59 g of palladium on carbon (10 wt. %), and 20 mL of THF. This mixture was stirred at room temperature under hydrogen for 12 h., and then removed solvent by evaporator. Into this flask, added 7.5 mL of hydrochloric acid aqueous solution (12 N) and 7.60 g (0.03 mol) of tetrachloro-1,4-benzoquinone, and 7 mL of ethanol. The portion of 5.30 g (0.03 mol) of 4-nitrocinamaldehyde was added slowly into the solution, and reacted at 90 °C for 3 days. The reactant was extracted from chloroform and organic layer was dried over anhydrous magnesium sulfate. The concentrated product solution was poured dropwise into hexane to precipitate the product. The crude solid was purified by the recrystallization from a mixture solvent of ethyl acetate and hexane, giving brown crystals (yield: 2.81 g, 29%).

mp 141-142 °C; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 3.04 (s, 3H, NCH<sub>3</sub>), 3.52 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.67 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 4.79 (t, 1H, OH), 6.89 (d, 2H, Ar-H), 7.67 (s, 5H, Ar-H), 7.41-8.42 (m, 6H, Ar-H), and 8.92 ppm (d, 1H, Ar-H).

Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub> (323.35): C, 66.9%; H, 5.3%; N, 13.0%. Found: C, 67.1%; H, 5.2%; N, 12.8%.

**Synthesis of 1-4-[(2-hydroxyethyl)(methylamino)phenyl]-1-ethanone (4a).** Into a 250 mL flask, added 20 g (144 mmol) of 4'-fluoroacetophenone, 20 mL of DMSO and 1.88 g (144 mmol) of cesium fluoride. This mixture was heated to 95 °C with stirring. The solution of 16.2 g (216 mmol) of **1** dissolved in 10 mL of DMSO, was added slowly into the reactant and maintained at that temperature for 24 h. This mixture was poured into cold water to precipitate yellow powder. The powder was separated by filtration and recrystallized from a mixture solvent of ethyl acetate and hexane, giving yellow crystals (yield: 18.7 g, 85%).

mp 69-70 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.43 (s, 3H, CH<sub>3</sub>), 3.04 (s, 3H, NCH<sub>3</sub>), 3.52 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.67 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 4.79 (t, 1H, OH), 6.80 (d, 2H, Ar-H), and 7.69 ppm (d, 2H, Ar-H).

**Synthesis of 2-[methyl-4-(6-nitro-4-phenyl-2-quinoly)anilino]-1-ethanol (5a, Qn2).** Into a 100 mL flask added 50 mL of acetic acid, 6 g (25 mmol) of 2-amino-5-nitro-benzo-

phenone, 5.0 g (26 mmol) of **4a**. This solution was stirred on heating. Into the solution added 5 mL of sulfuric acid and reacted at 100 °C for 24 h. The reactant was poured into 500 mL of diluted potassium hydroxide aqueous solution. The precipitated solid was washed with potassium hydroxide/ethanol solution at reflux. The product was finally purified by silica-gel column chromatography, yielding orange crystals (yield: 6.5 g, 65%).

mp 1820181 °C; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 3.04 (s, 3H, NCH<sub>3</sub>), 3.52 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 3.67 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 4.79 (t, 1H, OH), 6.78-6.83 (d, 2H, Ar-H), 7.63 (s, 5H, Ar-H), 8.03- 8.38 (m, 5H, Ar-H), and 8.54 ppm (d, 1H, Ar-H).

Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> (399.44): C, 72.2%; H, 5.3%; N, 10.5%. Found: C, 72.3%; H, 5.3%; N, 10.4%.

**Synthesis of 1-4-[di-(2-hydroxyethyl)amino]-phenyl-1-ethanone (4b).** Into a 250 mL flask added 20 mL of DMSO, 20g (114 mmol) of 4'-fluoroacetophenone, and 17.5 g (114 mmol) of cesium fluoride. Into this mixture added the solution of 18.2 g (173 mmol) of diethanol amine in 10 mL of DMSO at 95 °C with stirring and reacted for 24 h. The reactant was poured into water to precipitate the product. The crude solid was recrystallized from ethyl acetate, giving yellow crystals (yield: 12.7 g, 50%).

mp 107-109 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.43 (s, 3H, CH<sub>3</sub>), 3.52-3.67 (m, 8H, N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 4.79 (t, 1H, OH), 6.80 (d, 2H, Ar-H) and 7.69 ppm (d, 2H, Ar-H).

**Synthesis of 2-[(2-hydroxyethyl)-4-(6-nitro-4-phenyl-2-quinoly)anilino]-1-ethanol (5b, Qn3).** Into a 100 mL flask added 50 mL of acetic acid and 5 g (20.6 mmol) of 2-amino-5-nitro-benzophenone, 4.8 g (24.0 mmol) of **4b**. The solution was heated on stirring and reacted with 5 mL of sulfuric acid at 100 °C for 24 h. The reactant was poured into 500 mL of diluted potassium hydroxide aqueous solution. The precipitated solid was washed with potassium hydroxide/ethanol solution at reflux. The product was finally purified by silica-gel column chromatography, yielding brown solids (yield: 6.6 g, 75%).

mp 185-186 °C; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 3.52-3.67 (m, 8H, N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 4.79 (t, 1H, OH), 6.78-6.83 (d, 2H, Ar-H), 7.63 (s, 5H, Ar-H), 8.03-8.38 (m, 5H, Ar-H), and 8.54 ppm (d, 1H, Ar-H).

Anal. Calcd. for C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub> (429.47): C, 69.9%; H, 5.4%; N, 9.8%. Found: C, 69.6%; H, 5.2%; N, 9.7%.

**Synthesis of vinyl monomer (6).** Into a 100 mL flask, added 1.0 g (2.5 mmol) of **Qn2**, 50 mL of dimethylformamide, and 0.523 g (5.0 mmol) of methacryloyl chloride. The portion of 0.76 g (7.5 mmol) of triethylamine was added into the solution, and stirred at 50 °C under nitrogen. The mixture was poured into water, and the precipitated solid was separated by filtration and purified by column chromatography. The product was obtained as orange crystals (yield 1.0 g, 86%).

mp 187-189 °C; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 1.81 (s, 3H, CH<sub>3</sub>), 3.04 (s, 3H, NCH<sub>3</sub>), 3.74 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 4.25 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>O), 5.50 (s, 1H, CH<sub>2</sub>=), 5.95 (s, 1H, CH<sub>2</sub>=), 6.80 (d, 2H, Ar-H), 7.55 (s, 5H, Ar-H), and 7.90-8.60 ppm (m, 6H, Ar-H).

**Polymerization of PMMA-Qn2.** In 25 mL polymerization ampoule, added a vinyl monomer **Qn2**, 0.70 g (1.5 mmol) and methyl methacrylate 0.35 g (MMA, 3.5 mmol), and 1,1,2,2-tetrachloroethane (TCE), and 5.0 mol % of 2,2-azobisisobutyronitrile (AIBN). The oxygen in ampoule was removed by freeze-vacuum-thaw method to remove oxygen in ampoule. The polymerization was carried out at 60 °C for 48 h, and poured into methanol to precipitate polymer, and washed thoroughly with methanol. The polymers were dissolved in THF and reprecipitated in methanol to remove unreacted monomer or oligomers. The polymer was separated by filtration and dried in vacuum oven.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 0.8-1.2 (m, CH<sub>3</sub>), 1.6-2.2 (m, CH<sub>2</sub>), 3.0 (s, NCH<sub>3</sub>), 3.6 (m, OCH<sub>3</sub>, NCH<sub>2</sub>), 4.1 (s, OCH<sub>2</sub>), and 6.8 8.8 ppm (m, Ar-H).

**Polymerization of PE-Qn3.** In a 100 mL flask, added 1.0 g (2.33 mmol) of **Qn3** and 10 mL of 1,2-dichloroethane. The diacid chloride monomer, 6FBC (0.99 g, 2.33 mmol) was added into the solution at room temperature with stirring. Triethylamine (0.48 g, 4.66 mmol) was added for acid trapper. The polymerization was carried out at 70 °C for 24 h. The polymer solution was poured into 400 mL of methanol. The precipitated solid was purified by repeated precipitation.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 3.95 (m, NCH<sub>2</sub>), 4.50 (m, OCH<sub>2</sub>) and 6.8 8.6 ppm (m, Ar-H).

**Polymerization of PI-Qn1.** The synthesis of hydroxylated polyimide has been described in the literature.<sup>14</sup> In 100 mL flask added 0.90 g (1.16 mmol) of precursor polymer and 20 mL of THF to dissolve polymers. Into this polymer solution, added 0.75 g (2.32 mmol) of **Qn1** and 1.22 g (4.64 mmol) of triphenyl phosphine. Then, the solution of 0.94 g (4.64 mmol) of diisopropyl azodicarboxylate (DIAD) in 10 mL of THF was added slowly into polymer solution. The post reaction was carried out at room temperature for 6 h. The solution was poured into 400 mL of methanol to precipitate polymers. The precipitated solid was purified by repeated precipitation using THF as a solvent and diethyl ether as a nonsolvent.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): 2.8 (s, NCH<sub>3</sub>), 3.7 (s, NCH<sub>2</sub>), 4.4 (s, OCH<sub>3</sub>), 6.8 8.6 ppm (m, Ar-H).

**Polymerization of PI-Qn2.** **PI-Qn2** was synthesized by the post reaction of hydroxylated polyimide with **Qn2**, which was described above.

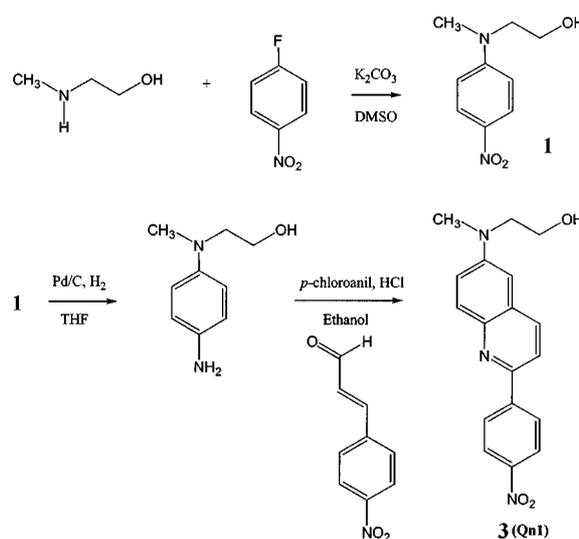
<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 2.8 (s, NCH<sub>3</sub>), 3.7 (s, NCH<sub>2</sub>), 4.4 (s, OCH<sub>3</sub>), 6.8 (s, Ar-H) and 7.08.6 ppm (m, Ar-H).

**Characterization and measurement.** FT-IR and <sup>1</sup>H-NMR (200 MHz) spectra were recorded on a Mattson Alpha Centauri spectrophotometer and a Varian Gemini 200 NMR spectrometer, respectively. Gel Permeation Chromatography (GPC) was performed by Waters HPLC system (model 510 pump, model 410 differential refractometer, PL Gel columns (HR2, HR4, HR5E)) using THF and polystyrene standards. Differential scanning calorimeter (DSC) was performed with a Dupont thermal analyzer DSC 2910 at a heating rate of 20 °C/min in nitrogen. Thermogravimetry (TG) was measured with a Dupont thermal analyzer DSC 2950 at a heating rate of 10 °C/min in nitrogen. UV-visible spectroscopy was performed by Shimadzu UV-240. The polymer film

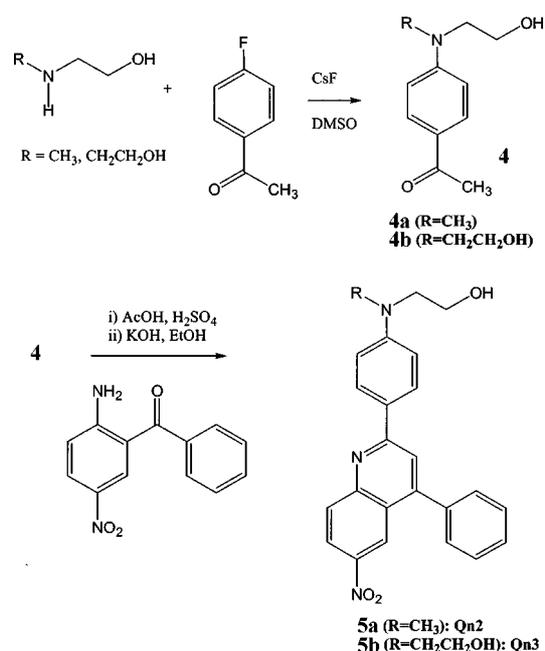
thickness was measured with a Tencor P-10 surface profiler. The second harmonic generation (SHG) coefficients, *d*<sub>33</sub> of corona poled films were determined by Maker-fringe method using a fundamental beam (1.064 μm) of Q-switched Nd:YAG laser. A quartz reference was used as a reference (*d*<sub>11</sub> = 0.5 pm/V). A detailed SHG measurements is described in the literature.<sup>22</sup> The electro-optic coefficients, *r*<sub>33</sub>, of electrode poled films were measured by the simple reflection technique proposed by C. C. Teng *et al.*<sup>15</sup> The electro-optic measurement procedure was reported by our recent literature in detail.<sup>16</sup>

## Results and Discussion

**Synthesis and properties of chromophores.** The synthetic



**Scheme 1.** Synthetic routes of a quinoline chromophore 1 (**Qn1**).



**Scheme 2.** Synthetic routes of quinoline chromophore 2 and 3 (**Qn2** and **Qn3**).

routes of three kinds of quinoline chromophores (**Qn1**~**Qn3**) were shown in Scheme 1 and Scheme 2, respectively. Two chromophores, **Qn1** and **Qn2** are monohydroxyethylated intermediates for the synthesis of a vinyl monomer for poly(methylmethacrylate) and a Mitsunobu reagent for polyimide, respectively. The third chromophore **Qn3** is a dihydroxyethylated monomer for the synthesis of polyester. The nitro compound (**1**) was synthesized by the cesium fluoride-catalyzed condensation reaction of 2-(methylamino)ethanol with fluoronitrobenzene, followed by the palladium-catalyzed reduction, giving an amino compound in quantitative conversion. The quinoline chromophore was synthesized by the Skraup reaction<sup>17</sup> and Friedlander reaction.<sup>18</sup> The quinoline chromophores such as **Qn2** and **Qn3** could be successfully synthesized by the general condensation reaction between acetophenone and *o*-benzoylaniline that have been used for the synthesis of aromatic polyquinolines. All the quinoline chromophores were well characterized by <sup>1</sup>H-NMR spectroscopy as well as elemental analysis.

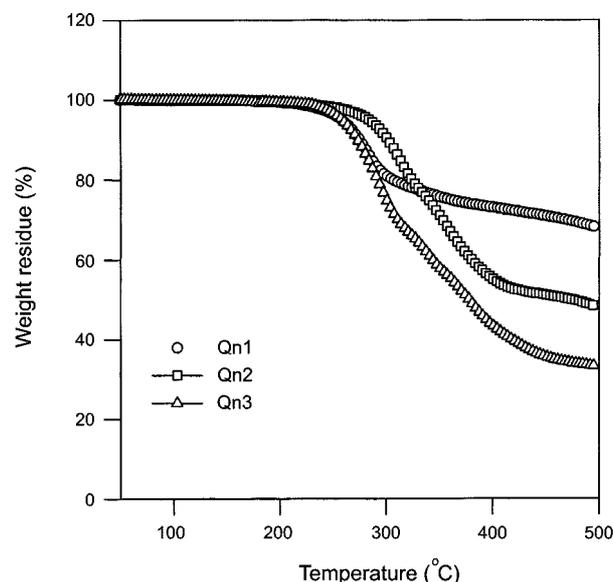
The representative physical properties of three chromophores were summarized in Table 1. In order to investigate nonlinear optical potentials of quinoline chromophores, we calculated their hyperpolarizability ( $\beta$ ) and dipole moment (D). It was well known that the higher values of  $D \times \beta$  is important for more active nonlinear optical properties. The hyperpolarizability ( $\beta$ ) of three chromophores was about  $24\text{--}27 \times 10^{-30}$  esu, which was a little lower value than that ( $34 \times 10^{-30}$  esu) of general stilbene chromophores. It is attributed to more stable chemical structure of quinoline itself with higher conjugation energy. This stable quinoline unit was expected to contribute for enhancement of thermal and photochemical properties of quinoline-based NLO polymers despite of lower NLO activities. The calculated dipole moment of **Qn1** was higher than that of **Qn2** and **Qn3**. As a result of MOPAC calculation, the **Qn1** was expected to be more advantageous for higher NLO activity than **Qn2**.

For a comparison of thermal stability, we carried out the thermogravimetric analysis of three quinoline compounds as shown in Figure 1. Three quinoline chromophores had almost the same initial decomposition temperatures of 250 °C. Among these, **Qn3** seemed to have the worst thermal stability due to perhaps thermally weak dihydroxylated structures. Comparing for thermal stability of **Qn1** structure with **Qn2**, the **Qn2** was expected to be more advantageous than **Qn1**. The

**Table 1.** The physical properties of three quinoline-based chromophores

	m.p. <sup>a</sup> (°C)	T <sub>d10</sub> <sup>b</sup> (°C)	$\lambda_{\max}$ <sup>c</sup> (nm)	D <sup>d</sup> (Debye)	$\alpha^d$ ( $\times 10^{-30}$ esu)	$\beta^d$ ( $\times 10^{-30}$ esu)
<b>Qn1</b>	142	274	428	9.0	5.9	24.4
<b>Qn2</b>	182	300	436	6.8	7.8	27.7
<b>Qn3</b>	185	273	437	6.8	7.8	27.7

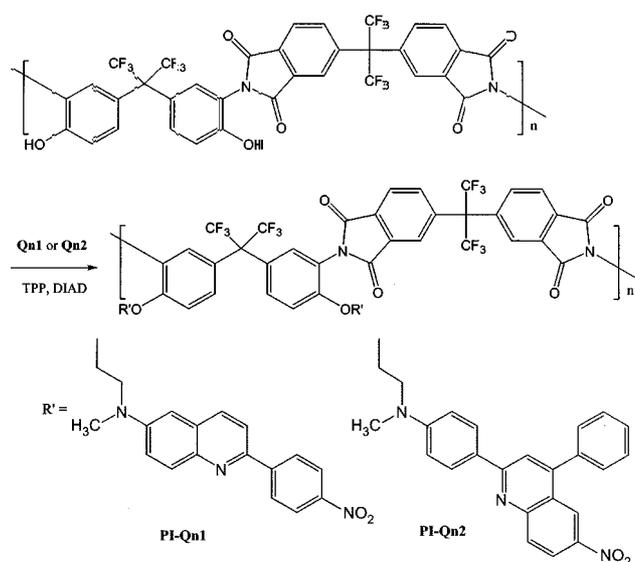
<sup>a</sup>Melting points were measured by DSC at a heating rate of 20 °C/min under N<sub>2</sub> atmosphere. <sup>b</sup>Ten percent weight loss temperatures were measured by TGA at a heating rate of 20 °C/min under N<sub>2</sub> atmosphere. <sup>c</sup>In solvent (THF). <sup>d</sup>Dipole moment (D) and hyperpolarizability ( $\beta$ ) were calculated by MOPAC 6.0.



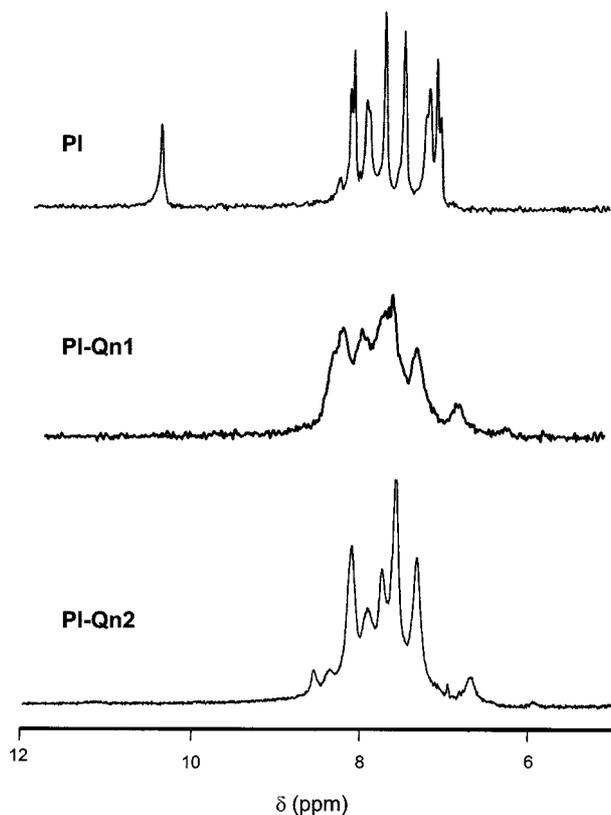
**Figure 1.** TGA curves of three quinoline chromophores.

maximum absorption wavelengths ( $\lambda_{\max}$ ) were around 428–437 nm, which were a little lower compared to stilbene chromophores.

**Polymerization and general properties of NLO polymers.** The structure of NLO polyimide with quinoline chromophores is displayed in Scheme 3. The **Qn1** was used for a grafting agent to hydroxylated polyimide through the Mitsunobu reaction. The precursor polyhydroxyimide was prepared by the conventional two-step procedure starting from **6FDAP** and **6FDA** through ring opening polyaddition and subsequent thermal cyclodehydration *in situ*. This precursor polyimide was highly soluble in THF adaptable enough for the Mitsunobu reaction. The <sup>1</sup>H-NMR characterization revealed that OH peak at 10.4 ppm was disappeared after the post Mitsunobu reaction, implying that quinoline chromophores were linked with the hydroxy groups (Figure 2). On the



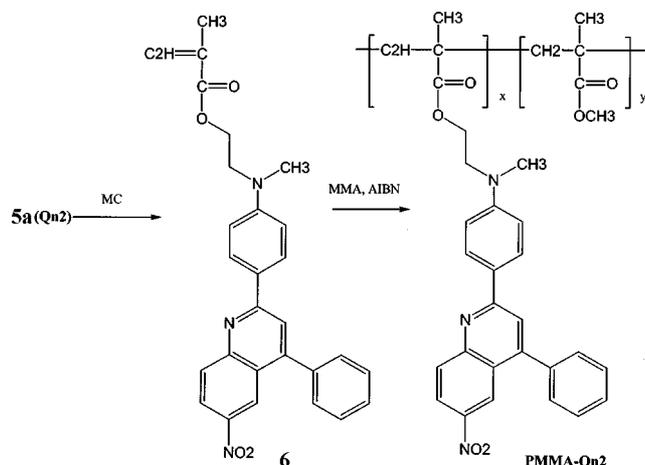
**Scheme 3.** Synthetic routes of NLO polyimides by Mitsunobu reaction (**PI-Qn1** and **PI-Qn2**).



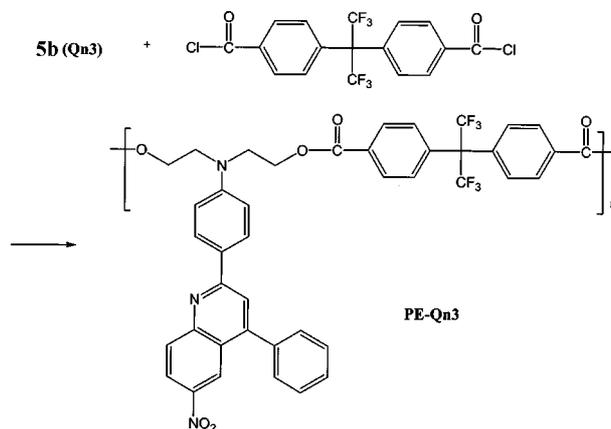
**Figure 2.**  $^1\text{H-NMR}$  spectra of polyimides before and after Mitsunobu reaction.

other hand, the second chromophore, **Qn2** was reacted with methacryloyl chloride to prepare a vinyl monomer. The resultant vinyl monomer was copolymerized with methyl methacrylate (MMA) with a feed ratio of 30/70 (NLO monomer/MMA), as shown the polymer structure in Scheme 4. The third compound, **Qn3** was polymerized with diacid chloride, giving NLO polyester as shown the structure in Scheme 5.

The physical properties of three polymers were summarized in Table 2. The weight-average molecular weight ( $M_w$ ) of PMMA copolymer was the highest of 44,000 among poly-



**Scheme 4.** Synthetic routes of a NLO polymethylmethacrylate copolymer (**PMMA-Qn2**).



**Scheme 5.** Synthetic routes of a NLO polyester (**PE-Qn3**).

**Table 2.** The physical properties of quinoline-based NLO polymers

Sample	$T_g^a$ ( $^{\circ}\text{C}$ )	$T_d^b$ ( $^{\circ}\text{C}$ )	$\lambda_{\text{max}}^c$ (nm)	$\lambda_{\text{cut-off}}^c$ (nm)	$M_n^d$	$M_w^d$	$M_w/M_n^d$
<b>PI-Qn1</b>	195	321	418	568	13,000	22,500	1.63
<b>PI-Qn2</b>	197	407	422	580	14,500	24,000	1.65
<b>PMMA-Qn2</b>	157	305	429	564	18,400	43,900	2.38
<b>PE-Qn3</b>	170	341	418	516	7,400	12,500	1.69

<sup>a</sup>Glass transition temperatures were measured by DSC at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. <sup>b</sup>Initial decomposition temperatures were measured by TGA at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. <sup>c</sup>In film. <sup>d</sup>Number-average and weight-average molecular weights were measured by GPC.

mers while that of polyester was the lowest of 12,500. The polyimides by the post-Mitsunobu reaction had the  $M_w$  in the range of 24,000. The  $M_w$  of a polyester was thought to insufficient  $M_w$  for manufacture of reliable optical waveguide, but the film was not brittle for a short period. The glass transition temperatures of three kinds of polymers measured by DSC, were 157  $^{\circ}\text{C}$  (PMMA), 170  $^{\circ}\text{C}$  (polyester), and 195  $^{\circ}\text{C}$  (polyimide), respectively. The thermogravimetric curves of three polymers are shown in Figure 3. The initial decomposition temperatures were measured to be at least above 300  $^{\circ}\text{C}$  at all NLO polymers. The polyimide with **Qn2** had better thermal stability than that with **Qn1**, and this result was in good agreement with the TGA result of NLO chromophores in Figure 1.

**SHG and EO properties of NLO polymers.** These polymers was dissolved in tetrachloroethane in a concentration of 10 wt%, and the solution was filtered by using 0.45  $\mu\text{m}$  microfilter syringe, and casted on glass for corona poling or indium tin oxide (ITO)-coated glass for contact poling, respectively. The films were dried at 100  $^{\circ}\text{C}$  in vacuum oven. The film thickness measured by Tencor surface profiler, were in the range of 0.1–0.2  $\mu\text{m}$ . The film for corona poling was placed on aluminum plate and tungsten wire as cathode was placed with a distance of about 1 cm on the film. The poling field was about 5–8 kV (current: <0.1 mA) at around glass transition temperatures of each polymers. On the other hand, the top electrode was prepared by gold evaporation on the film, and contact-poled between ITO and

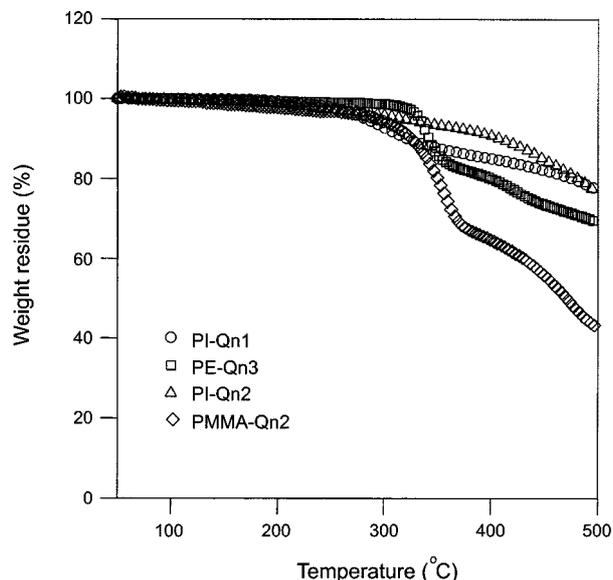


Figure 3. TGA curves of three NLO polymers.

Table 3. Second harmonic coefficients ( $d_{33}$ ) of NLO-polymers

Sample	$d_{31}$	$d_{33}^a$	$d_{33}/d_{31}$	O.P. <sup>b</sup>
PI-Qn1	0.89	2.7	3.0	0.15
PI-Qn2	0.99	3.1	3.1	0.17
PMMA-Qn2	7.6	27.5	3.6	0.27

<sup>a</sup>Measured using Nd-YAG laser (1064 nm). <sup>b</sup>Order Parameter  $\Phi = 1 - A_p/A_0$ .

gold electrodes in an electric field of 0.2-0.8 MV/cm. The poling was carried out at 10 °C lower temperature than their glass transition temperatures.

First, in order to investigate the alignment of NLO chromophores, we measured their order parameter from UV-visible spectra of the corona-poled films. Table 3 summarized the order parameters and second harmonic generation (SHG) coefficients of **PMMA-Qn2**, **PI-Qn1** and **PI-Qn2**, respectively. A Polyester film after corona-poling was somewhat damaged so we could not measure its SHG coefficient. We could observe that the polyimide films were hardly aligned on poling even at high electric field while a PMMA film was aligned with an order meter of about 0.27. Accordingly, polyimide had very low SHG coefficient ( $d_{33}$ ) of about 3 pm/V. This low NLO activity might be ascribed to the alignment difficulty due to high glass transition temperature of polyimide as well as rod-like structure of NLO chromophore. However, the  $d_{33}$  of **PMMA-Qn2** was mea-

Table 4. Electro-optic coefficients ( $r_{33}$ ) of NLO polymers

Sample	$r_{33}^a$ (pm/V)	$r_{33}^b$ (pm/V)
PI-Qn1	1.9	–
PI-Qn2	2.1	–
PMMA-Qn2	15.1	6.8

<sup>a</sup>Measured at a wavelength of 632 nm. <sup>b</sup>Measured at a wavelength of 1300 nm.

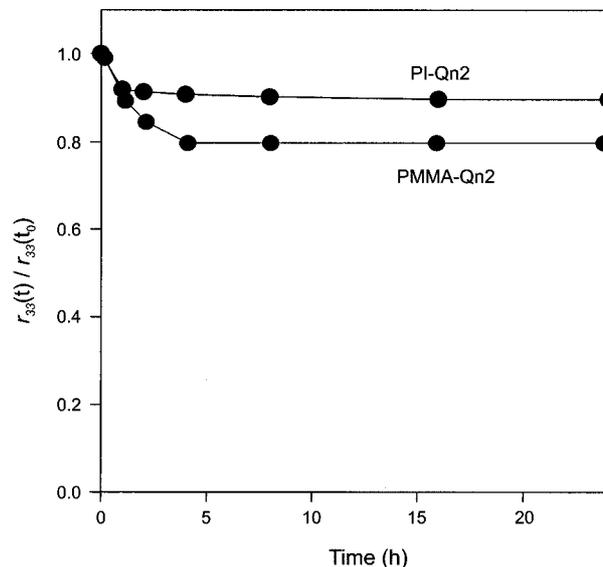


Figure 4. Temporal stability of electro-optic coefficient at 80 °C.

sured to be 28 pm/V. From this SHG measurement, we could confirm the NLO potential activity of quinoline-based NLO polymer despite of a little lower NLO activity compared to that of general stilbene-based polymers. Using contact-poled films, we measured the electro-optic coefficients ( $r_{33}$ ) of **PMMA-Qn2** and **PI-Qn2**, respectively. As like the SHG results, the **PMMA-Qn2** exhibited higher  $r_{33}$  of 15 pm/V at a wavelength of 635 nm while **PI-Qn2** exhibited lower  $r_{33}$ . However, the temporal stability of  $r_{33}$  at 80 °C was more stable at polyimide system than at PMMA system as shown the relaxation behavior of  $r_{33}$  in term of short period in Figure 4.

## Conclusions

Three kinds of quinoline chromophores were synthesized in order to obtain more thermally stable NLO chromophores than general stilbene-based chromophores. NLO active poly-(methylmethacrylate), polyester, and polyimide were synthesized by using these quinoline-based NLO chromophores, respectively. The enhanced thermal stability of quinoline chromophores themselves and polymers therefrom was verified by TG analysis. The glass transition temperatures of NLO polymers detected by DSC were in the range of 140-195 °C depending on polymer backbones structure. From the SHG and EO coefficient of quinoline-based PMMA copolymers, had an  $r_{33}$  of 15 pm/V (at 635 nm) and 6 pm/V (at 1300 nm). Polyimide system was difficult to achieve high NLO properties due to high glass transition temperature, however, showed more temporally stable behavior than PMMA system.

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