

## Notes

### Synthesis and Nonlinear Optical Properties of Novel Y-type Polyimide Containing Dioxynitroazobenzene Group

Mi Sung Kim, Byeongman Jeon, and Ju-Yeon Lee\*

Institute of Basic Science, Department of Chemistry, Inje University, Gimhae 621-749, Korea. \*E-mail: chemlly@inje.ac.kr  
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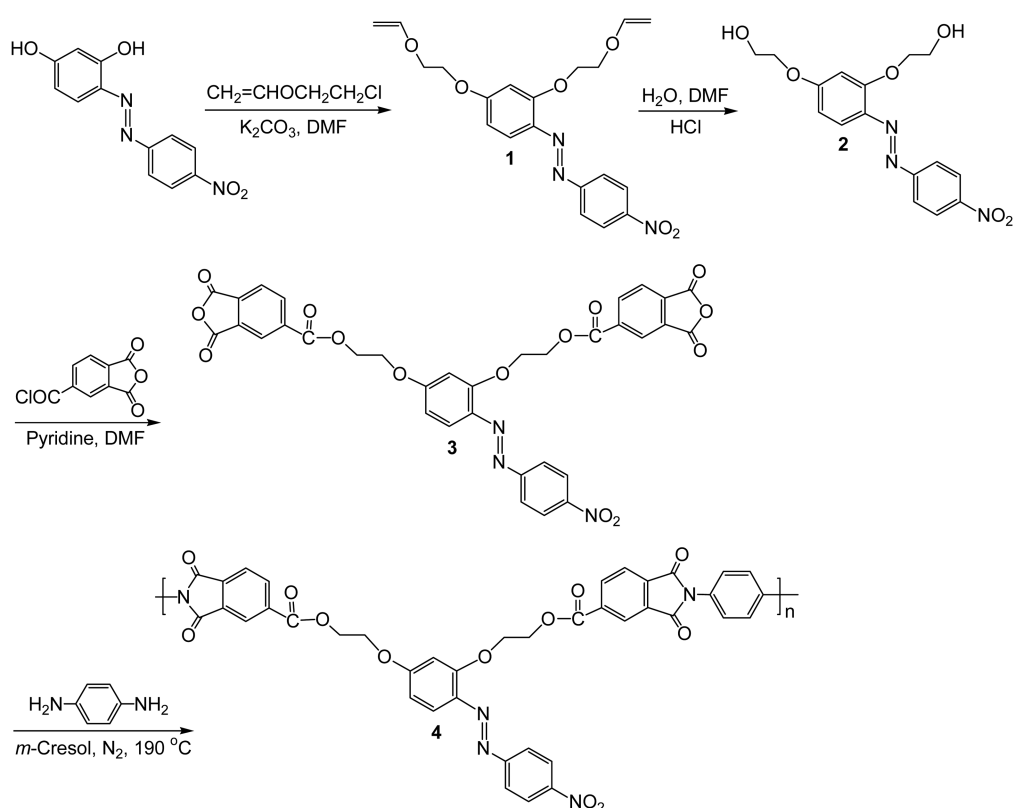
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Recently, great attention has been focused on the synthesis of nonlinear optical (NLO) materials because of their potential applications in the field of electro-optic devices including ultrafast optical switches and high-speed optical modulators.<sup>1-4</sup> NLO polymers have many advantages superior to conventional inorganic ones such as low cost, ultrafast response, wide response wave band, and good processability to form optical devices. One of the current challenges is to design novel NLO polymers having optimized properties. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with a high glass transition temperature ( $T_g$ ). In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linked systems<sup>5,6</sup> and the utilization of polymers with high glass transition temperature ( $T_g$ ) such as polyimides.<sup>7-10</sup> Polyimide materials for NLO applications have attracted attentions because of their high  $T_g$  and high thermal stability, which can be used to stabilize the dipole orientation of the NLO chromophore at high temperatures. Various type of polyimide-based NLO materials have been synthesized, and their properties have been studied.<sup>7-10</sup> There are two types of NLO polyimides, which have been used either as host polymers for composite materials or as matrix polymer backbones for side-chain NLO chromophores. Main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable noncentrosymmetric films. Side-chain NLO polymer systems have the advantages such as good solubility and homogeneity, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we prepared novel NLO polyimides containing dioxynitrostilbenyl groups<sup>11-13</sup> and dioxynitrobenzylidenemalononitrile<sup>14-17</sup> as NLO chromophores. The resulting polymers exhibit enhanced thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophores. In this work reported here, we prepared new Y-type poly-

imide containing nitrophenylazoresorcinoy groups as NLO chromophores. We selected the latter as NLO chromophores because they were expected to have high optical nonlinearities. Furthermore, these groups constitute novel Y-type NLO polyimides, and these Y-type NLO polyimides have not yet been reported in the literature. Thus, we synthesized a new type of NLO polyimide, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-type NLO polymer is expected to have the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties such as solubility, thermal stability, and SHG activity.

#### Results and Discussion

Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 4-(4-nitrophenylazo)resorcinol. Compound **2** was prepared by acid-catalyzed hydrolysis of **2** in DMF. Dianhydride monomer **3** was prepared by the reaction of diol **2** with trimellitic anhydride acid chloride in dry DMF in the presence of pyridine. Polyimide **4** was synthesized through the reaction of aromatic dianhydride monomer **3** containing NLO chromophore with equivalent amount of 1,4-phenylenediamine in *m*-cresol. The synthetic route for polymer **4** is presented in Scheme 1. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by <sup>1</sup>H NMR, IR spectra, and elemental analysis. <sup>1</sup>H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer **4** shows peaks near 1779 and 729 cm<sup>-1</sup> that are characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. The spectrum also shows strong absorption peaks near 1723 cm<sup>-1</sup> and 1369 cm<sup>-1</sup> due to symmetric carbonyl stretching and C-N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO chromophores remained intact during the polymerization. The molecular weights were determined by GPC using polystyrene as the standard and THF as an eluent. The



**Scheme 1.** Synthetic scheme and structure of polymer **4**.

number average molecular weight ( $M_n$ ) of the polymer **4**, determined by GPC, was  $14,800 \text{ g mol}^{-1}$  ( $M_w/M_n=1.78$ ). The polymer **4** is soluble in common solvents such as DMF and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is  $0.30 \text{ dL g}^{-1}$ . The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polyimide, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility. Thus, we obtained a new NLO polyimide with side-chain and main-chain characteristics. Having obtained the well defined Y-type polyimide **4**, we investigated its properties.

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. Polymer **4** has a thermal stability up to  $290 \text{ }^\circ\text{C}$  according to its TGA thermogram. The  $T_g$  value of the polymer **4** measured using DSC is near  $128 \text{ }^\circ\text{C}$ . This  $T_g$  value is lower than those of the polyimide **5** (see Scheme 2) containing dioxynitrostilbene, which is near  $162 \text{ }^\circ\text{C}$ ,<sup>13</sup> or dioxybenzylidenemalononitrile, which is near  $188 \text{ }^\circ\text{C}$ .<sup>15</sup> The lower  $T_g$  value is probably due to the easy *cis-trans* isomerization of diazo linkage.

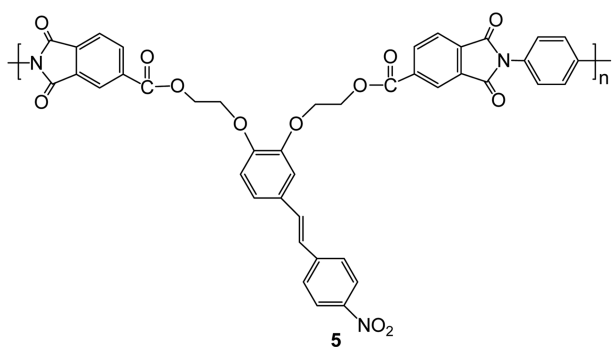
The NLO properties of polymers were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually to  $5\text{--}10 \text{ }^\circ\text{C}$  higher than  $T_g$ , a

**Table 1.** Thermal Properties of Polymer **4**

Polymer	$T_g^a$ , $^\circ\text{C}$	Degradation temp, $^\circ\text{C}^b$			$M_n^c$	$M_w^c$
		5 wt %- Loss	20 wt %- Loss	40 wt %- Loss		
<b>4</b>	128	300	403	536	14,800	26,300
<b>5<sup>d</sup></b>	162	375	435	538	22,500	39,100

<sup>a</sup>Determined from DSC curves measured with a TA 2920 differential scanning calorimeter with a heating rate of  $10 \text{ }^\circ\text{C/min}$  under nitrogen atmosphere. <sup>b</sup>Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of  $10 \text{ }^\circ\text{C/min}$  under nitrogen atmosphere. <sup>c</sup>Measured by gel permeation chromatography (GPC) in THF using polystyrene standard. <sup>d</sup>Polyimide containing 3,4-dioxynitrostilbene.<sup>13</sup>

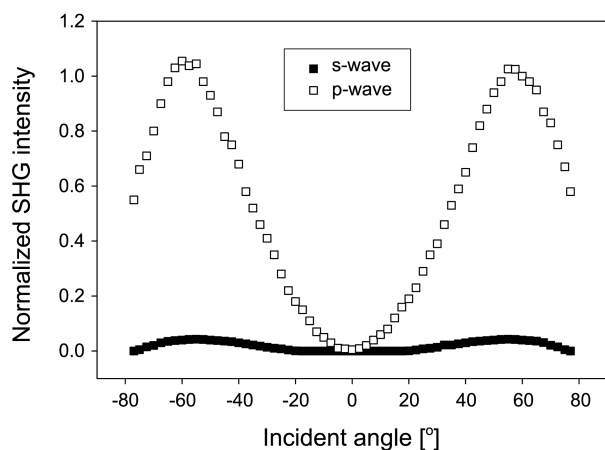
corona voltage of  $6.5 \text{ kV}$  was applied and this temperature was maintained for 30 min. The refractive index of the sample was measured using the optical transmission technique.<sup>18</sup> The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of  $1064 \text{ nm}$  with a mode locked Nd-YAG laser and OPO. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 1 shows the angular dependence of SHG signal for a poled sample of polymer **4**. The SHG values were compared with those obtained from a Y-cut quartz plate. To calculate the  $d_{31}$  and  $d_{33}$  values, both *s*-polarized and *p*-polarized IR laser were directed at the



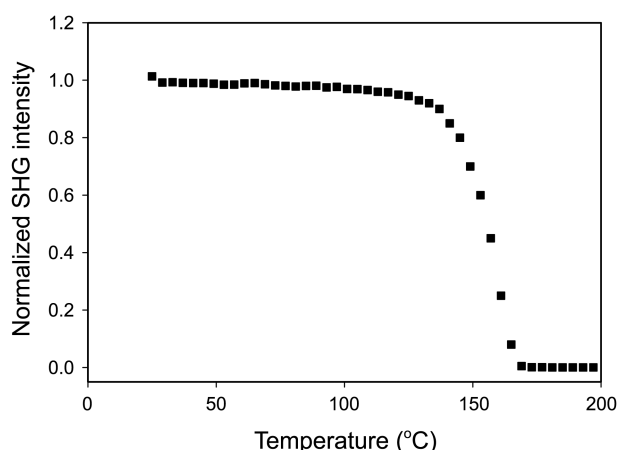
**Scheme 2.** Structure of polymer 5.

samples. The NLO properties of polymer 4 are summarized in Table 2. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.<sup>19</sup> The values of  $d_{31}$  and  $d_{33}$  for polymer 4 are  $1.72 \times 10^{-9}$  and  $5.46 \times 10^{-9}$  esu, respectively. This  $d_{33}$  value is similar with that of polyimide with dioxybenzylidenemalononitrile, which is near  $5.48 \times 10^{-9}$  esu,<sup>15</sup> but is higher than that of the polyimide 5 containing dioxynitrostilbene, which is near  $4.63 \times 10^{-9}$  esu,<sup>13</sup> or that of polyester containing dioxynitroazobenzene, which is near  $4.53 \times 10^{-9}$  esu.<sup>4</sup> Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is no resonant contribution to this  $d_{33}$  value. In the isotropic model, the ratio of  $d_{33}/d_{31}$  is predicted to be about 3. Our  $d_{33}/d_{31}$  value of 3.17 is in good agreement with the predicted value.

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. Figure 2 shows the dynamic thermal stability study of the NLO activity of a film of polymer 4. To investigate the real time NLO decay of the SHG signal of the poled polymer film as a function of temperature, *in situ* SHG measurement was performed at a heating rate of  $4 \text{ }^\circ\text{C min}^{-1}$  from 30 to  $200 \text{ }^\circ\text{C}$ . The polymer film exhibits a thermal stability up to  $T_g$ , and no significant SHG decay is observed below  $130 \text{ }^\circ\text{C}$ . This SHG thermal stability is lower than that of the polyimide 5 containing dioxynitrostilbene, which is in the range 180-190



**Figure 1.** Angular dependence of SHG signal for a poled film of polymer 4.

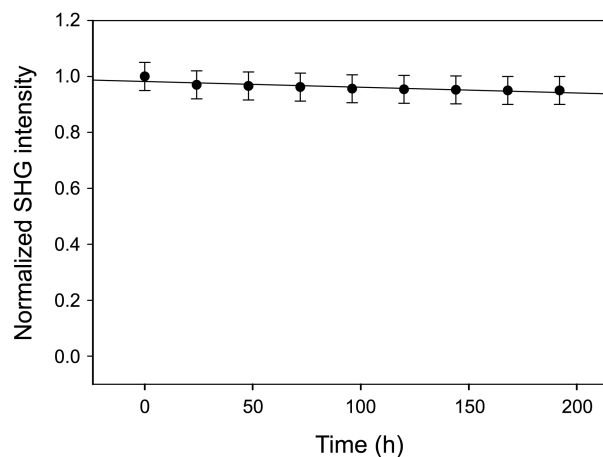


**Figure 2.** Normalized SHG signal of polymer 4 as a function of temperature at a heating rate of  $4 \text{ }^\circ\text{C/min}$ .

$^\circ\text{C}$ <sup>13</sup> or dioxybenzylidenemalononitrile, which is in the range 190-200  $^\circ\text{C}$ .<sup>15</sup> The lower SHG thermal stability of the polymer 4 is probably due to the lower  $T_g$  value. However, The SHG thermal stability of polymer 4 is higher than that of the polyester containing dioxynitroazobenzene, which is near  $120 \text{ }^\circ\text{C}$ .<sup>4</sup> In Figure 3, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours. In general, side chain NLO polymers lose the thermal stability of dipole alignment below  $T_g$ . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The high thermal stability of second harmonic generation of polymer 4 is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure. Thus, we obtained a new NLO polyimide having the characteristics of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

## Experimental Section

**Materials.** 4-(4-Nitrophenylazo)resorcinol, 2-chloroethyl vinyl ether, trimellitic anhydride chloride, and 1,4-phenyl-



**Figure 3.** Normalized SHG signal of polymer 4 as a function of baking time at  $80 \text{ }^\circ\text{C}$  in air.

**Table 2.** Nonlinear Optical Properties of Polymer 4

Polymer	$d_{33}^a$ (esu)	$d_{31}^a$ (esu)	film thickness <sup>b</sup> ( $\mu\text{m}$ )	$d_{31}/d_{33}$	$n$
<b>4</b>	$5.46 \times 10^{-9}$	$1.72 \times 10^{-9}$	0.54	3.17	1.716
<b>5<sup>c</sup></b>	$4.53 \times 10^{-8}$	$1.66 \times 10^{-9}$	0.60	2.73	1.724

<sup>a</sup>SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>19</sup> <sup>b</sup>Film thickness was determined using the optical transmission technique.<sup>18</sup> <sup>c</sup>Polyimide containing 3,4-dioxynitrostilbene.<sup>13</sup>

enediamine (PDA) were used as received. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium hydride, followed by distillation under reduced pressure. *m*-Cresol was dried over calcium chloride, and then over 4 Å molecular sieves, and it was distilled under reduced pressure before use. 2,4-Di-(2'-vinylxyethoxy)-4'-nitroazobenzene (**1**) and 2,4-di-(2'-hydroxyethoxy)-4'-nitroazobenzene (**2**) were prepared according to a literature procedure.<sup>4</sup>

**Measurements.** Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. <sup>1</sup>H NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer.  $T_g$  values were measured using a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer (TGA) with a heating rate of 10 °C min<sup>-1</sup> up to 800 °C was used for the thermal degradation of polymers under nitrogen. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the polymers were estimated using gel permeation chromatography (styragel HR5E4E columns; THF solvent). The alignment of the NLO chromophore of the polymer was carried out by corona poling method. The refractive index of the sample was measured using the optical transmission technique.<sup>18</sup> SHG measurements were made using a Maker fringe technique.<sup>19</sup>

**Preparation of 2,4-Bis(3,4-dicarboxyphenylcarboxyethoxy)-1-(4-nitrophenylazo)benzene dianhydride (3).** Compound **2** (3.47 g, 0.01 mol) was dissolved in dry DMF (20 mL) and pyridine (20 mL) at 50 °C under nitrogen. Trimellitic anhydride chloride (8.42 g, 0.04 mol) was added to the mixture with stirring under at 50 °C. The resulting solution was stirred for 12 h at room temperature. The resulting solution was diluted with 250 mL of water and stirred for 1 h to dissolve pyridine hydrochloride. The product was filtered, and washed successively with water and methanol. Thus obtained deep brown product was dried at 50 °C under vacuum to give 4.86 g (70% yield) of pure **3**. <sup>1</sup>H NMR (DMSO- $d_6$ ) 4.42-4.82 (t, 8H, 2 -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.68-6.83 (m, 1H, aromatic), 6.85-7.12 (m, 1H, aromatic), 7.44-7.56 (t, 1H, aromatic), 7.65-8.08 (m, 4H, aromatic), 8.15-8.47 (m, 5H, aromatic), 8.68 (s, 1H, aromatic). IR (KBr) 3079 (w,

=C-H), 2929 (w, C-H), 1724 (vs, C=O, ester), 1600 (s, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>21</sub>N<sub>3</sub>O<sub>14</sub>: C, 58.71; H, 3.04; N, 6.04. Found: C, 58.82; H, 3.12; N, 6.11.

**Synthesis of Polymer 4.** The polymerization was carried out in a drybox at room temperature. A representative synthetic procedure was as follows. Anhydride **3** (6.95 g, 0.01 mol) was added slowly to a solution of 1,4-phenylenediamine (1.08 g, 0.01 mol) in 60 mL of dry *m*-cresol over 1 h. The polymerization was allowed to continue at 50 °C for 12 h. The mixture was gradually elevated to 190 °C and then stirred for 12 h. The polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected and further purified by extraction in a Soxhlet extractor with diethyl ether. The final product was dried under vacuum to give 6.90 g (90% yield) of polymer **4**. Inherent viscosity ( $\eta_{inh}$ ): 0.30 dL g<sup>-1</sup> ( $c = 0.5$  g dL<sup>-1</sup> in *m*-cresol at 25 °C). <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  4.08-4.86 (m, 8H, 2 -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.34-7.45 (m, 6H, aromatic), 7.56-7.68 (m, 2H, aromatic), 7.75-8.56 (m, 9H, aromatic). IR (KBr) 2960 (w, C-H), 1779 (m, C=O), 1723 (vs, C=O), 1612 (s, C=C), 1369 (s, C-N), 729 (s, imide ring) cm<sup>-1</sup>. Anal. Calcd for (C<sub>40</sub>H<sub>25</sub>N<sub>5</sub>O<sub>12</sub>)<sub>n</sub>: C, 62.58; H, 3.28; N, 9.12. Found: C, 62.67; H, 3.36; N, 9.20.

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