

# Articles

## An Alternate Synthetic Approach for Soluble Nonlinear Optical Polyimides

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Three functionalized second-order nonlinear optical polyimides were synthesized by the step growth polymerization reaction between a chromophore-containing dianhydride and three different diamine compounds. This alternate approach (i.e., incorporating a nonlinear chromophore into a dianhydride monomer) may avoid troublesome syntheses of the chromophore-containing diamine and can provide easy preparation of the polyimides with various chromophores. The number-average molecular weights ( $M_n$ ) of final polymers determined by GPC ranged between 10 000 and 16 800 ( $M_w/M_n = 1.59-2.28$ ). No melting was detected and they showed relatively low glass-transition temperatures ranging from 161 to 181 °C. They are readily soluble in aprotic polar solvents such as tetrahydrofuran, *N,N*-dimethylformamide, *N*-methylpyrrolidinone, and so forth. High optical quality films were prepared by spin casting from a 10 wt % cyclohexanone or *N*-methylpyrrolidinone solution. The second harmonic generation (SHG) coefficients,  $d_{33}$ , of the polymers were determined to be 24–37 pm/V ( $d_{33}(\infty) = 7-10$  pm/V) at a fundamental wavelength of 1064 nm. All of the poled polymer samples showed outstanding orientational stability up to 125 °C without any measurable decay of the SHG signal. In particular, the polyimide with a 4,4'-(hexafluoroisopropylidene)dianiline unit (PI-2-DANS) showed the best dynamical thermal stability of the poling-induced dipole alignment up to ca. 170 °C.

### Introduction

One of the problems to be overcome with regard to the practical application in nonlinear optical (NLO) polymeric systems is the relaxation of the aligned dipoles at high temperatures.<sup>1</sup> To improve thermal and temporal stability, several approaches have been tried, in particular using cross-linked polymers<sup>2,3</sup> and/or high glass-transition temperature systems.<sup>4-7</sup> A combination of a cross-linked and high glass-transition system has

also been reported.<sup>8</sup> Recently, much attention has been focused on processible high glass-transition temperature NLO thermoplastic polymers.<sup>9</sup> Among these thermostable polymers, functionalized aromatic polyimides have attracted much attention because of their high-temperature alignment stability, good mechanical properties, low optical loss, and so forth. Several synthetic routes for NLO-functionalized polyimides have been reported. The first use of polyimides as nonlinear optical materials was with guest/host systems.<sup>10,11</sup> Problems such as rapid relaxation of poling-induced order, limited loading levels of the chromophores, and sublimation of the chromophores during the harsh imidization process

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led to the incorporation of NLO chromophores into the polyimide backbone to give better NLO thermal stability.

A common synthetic route for NLO polyimides is the condensation polymerization of dianhydrides with diamines containing an NLO chromophore via a poly(amic acid) prepolymer.<sup>12</sup> This method, however, often involves a tedious synthesis of the chromophore-containing diamine monomers. Sometimes, the fact that few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis limits the kind of chromophores that incorporate in the polyimide backbone.<sup>13</sup> To avoid the synthesis of chromophore-containing diamine compounds, an alternate synthetic route was developed by Jen et al.<sup>13,14</sup> They developed one-pot preparation of a preimidized, hydroxy-containing polyimide, followed by the covalent attachment of a chromophore to the backbone of the polyimide via a polymer analogous Mitsunobu reaction. This approach allows some flexibility in the selection of the polymer backbone and the chromophores. However, in this work the NLO chromophore was incorporated into the polyimide backbone only through a single bonding site, which can reduce the orientational stability at high temperatures relative to chromophores attached via multiple bonding sites. In addition, one-step polymerization between an NLO chromophore-containing diol and a bis-imide compound via a Mitsunobu reaction was reported by the authors.<sup>15</sup> Using this method, there is no need to synthesize NLO-diamine monomers. This material however was produced with relatively low molecular weights because of poor solubility of the polymer. To overcome the problems such as poor polymer solubility, relaxation of aligned dipoles at elevated temperatures, and difficult syntheses of chromophore-containing diamine monomers, a new synthetic approach is described. In the present investigation, we incorporate an NLO active chromophore into the dianhydride unit instead of the diamine unit. This new approach avoids the troublesome NLO-diamine synthesis. This technique also permits the versatility in selection of the chromophores to be incorporated into the polyimide backbone in addition to providing two bonding sites for chromophore attachment to give better orientational stability. To improve solubility of these materials, we introduced an ether linkage into the polymer backbone and used a flexible diamine monomer.

In this report, an alternate synthetic route for the preparation of NLO-functionalized polyimides from the polycondensation reaction between a chromophore-containing dianhydride monomer and three diamine monomers is presented. We will discuss physicochemical and optical characterization of these new polyimide structures and the details of their optical second-order activity in terms of electric field poling, and temporal stability along with thermal stability.

## Experimental Section

**Materials.** Anhydrous *N*-methylpyrrolidinone (NMP), *p,p'*-diaminodiphenylmethane (DAPM), and 4,4'-(hexafluoroisopropylidene)dianiline (HFPA) were purchased from Aldrich Chemical Co. and used as received. 4-Bis(hydroxyethyl)amino-4'-nitrostilbene (**1**) and 4-bis(aminoethyl)amino-4'-nitrostilbene (BANS) were synthesized according to the method described in the literature.<sup>6,16</sup> Pyridine dried with Linde-type 4 Å molecular sieves was used without distillation. All other solvents and reagents were analytical-grade quality, purchased commercially, and used without any further purification.

**Monomer Synthesis.** 4-Bis(methylsulfonyloxy)ethylamino-4'-nitrostilbene (**2**). To a 250 mL two-necked flask containing compound **1** (2.00 g, 6.09 mmol), methanesulfonyl chloride (1.74 g, 15.23 mmol), and methylene chloride (80 mL) was added triethylamine (1.67 g, 16.44 mmol) dropwise in the ice bath. The mixture was stirred for 3 h at ambient temperature. After water was added to the reaction mixture, the mixture was washed with water several times. The organic layer was dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The red crude product was recrystallized from methylene chloride to yield a bright red solid. The product was filtered and dried in a vacuum desiccator. The product yield was 2.60 g (88.0%): mp 157 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 3.16 (s, 6H, -SO<sub>2</sub>CH<sub>3</sub>), 3.79 (t, 4H, -NCH<sub>2</sub>CH<sub>2</sub>-OMs), 4.33 (t, 4H, -NCH<sub>2</sub>CH<sub>2</sub>OMs), 6.85 (d, 2H, Ar H), 7.15 (d, 1H, vinyl proton), 7.43 (d, 1H, vinyl proton), 7.53 (d, 2H, Ar H), 7.77 (d, 2H, Ar H), 8.18 (d, 2H, Ar H). Anal. Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: C, 49.57; H, 5.00; N, 5.78; S, 13.23. Found: C, 49.23; H, 4.87; N, 5.81; S, 13.04.

4-Bis[3,4-bis(methoxycarbonyl)phenoxy]ethylamino-4'-nitrostilbene (**3**). To a solution of compound **2** (2.00 g, 4.13 mmol) and 4-hydroxyphthalic acid dimethyl ester (1.74 g, 8.26 mmol) in 100 mL of *N,N*-dimethylformamide (DMF) was added potassium carbonate (1.43 g, 10.33 mmol). The solution was stirred overnight at around 70 °C. The reaction mixture was cooled to room temperature and water was added. Extraction with methylene chloride and evaporation under reduced pressure gave a dark red liquid. This solution was added to cold water dropwise to yield a bright red solid. After being washed with water several times, it was dried at 40 °C in a vacuum oven for 4 h and 2.79 g (95.0%) of the pure product was obtained: mp 73 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 3.84 (s, 6H, -CO<sub>2</sub>CH<sub>3</sub>), 3.87 (s, 6H, -CO<sub>2</sub>CH<sub>3</sub>), 3.92 (t, 4H, -NCH<sub>2</sub>-CH<sub>2</sub>O-), 4.23 (t, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 6.76 (d, 2H, Ar H), 6.93 (m, 3H, Ar H), 7.02 (d, 2H, Ar H), 7.18 (d, 1H, vinyl proton), 7.44 (d, 2H, Ar H), 7.55 (d, 2H, Ar H), 7.76 (d, 2H, Ar H), 8.16 (d, 2H, Ar H). Anal. Calcd for C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>12</sub>: C, 64.03; H, 5.10; N, 3.93. Found: C, 64.13; H, 5.13; N, 3.99.

4-Bis[3,4-dicarboxyphenoxy]ethylamino-4'-nitrostilbene (**4**). To a two-necked flask containing compound **3** (2.00 g, 2.81 mmol) and acetone (100 mL) was added sodium hydroxide (0.67 g, 16.86 mmol) dissolved in 50 mL of water. The mixture was hydrolyzed at ca. 60 °C overnight and cooled to room temperature. Adding the reaction mixture into an aqueous hydrogen chloride solution dropwise yielded a bright red solid. The crude red solid was recrystallized from ethyl acetate to yield the tetraacid, 1.66 g (90.1%): mp 139 °C. <sup>1</sup>H NMR (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 4.27 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 6.89 (d, 2H, Ar H), 7.06 (m, 4H, Ar H), 7.13 (d, 1H, vinyl proton), 7.43 (d, 1H, vinyl proton), 7.46 (d, 2H, Ar H), 7.68 (d, 2H, Ar H), 7.76 (d, 2H, Ar H), 8.17 (d, 2H, Ar H), 12.85 (br s, 4H, -CO<sub>2</sub>H). Anal. Calcd for C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>O<sub>12</sub>: C, 62.19; H, 4.31; N, 4.27. Found: C, 62.89; H, 4.65; N, 4.12.

4-Bis[1,3-dioxisobenzofuran-5-yloxy]ethylamino-4'-nitrostilbene (**5**). Compound **4** (2.00 g, 3.05 mmol) was dissolved in 30 mL of acetic acid and 30 mL of acetic anhydride was added to the solution. The mixture was dehydrated at ca. 125 °C for 6 h and then cooled to room temperature. The precipitated dark brown solid was filtered and washed in hot methanol to remove undesired impurities. The product was filtered and

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dried under reduced pressure and 1.40 g (74.1%) of the dianhydride monomer was obtained: mp 177 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 3.95 (t, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 4.42 (t, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 6.90 (d, 2H, Ar H), 7.13 (d, 1H, vinyl proton), 7.47 (m, 7H, Ar H), 7.76 (d, 2H, Ar H), 7.95 (d, 2H, Ar H), 8.17 (d, 2H, Ar H). Anal. Calcd for C<sub>34</sub>H<sub>24</sub>N<sub>2</sub>O<sub>10</sub>: C, 65.80; H, 3.91; N, 4.51. Found: C, 65.21; H, 4.05; N, 4.53.

**Polymer Synthesis. Polymer PI-1-DANS.** After the setup was purged with nitrogen for 15 min, *p,p'*-diaminodiphenylmethane (0.16 g, 0.81 mmol) and anhydrous NMP (3.5 mL) were added in a 25 mL two-necked flask. The solution was stirred at 0 °C until diamine dissolved completely and the dianhydride monomer 5 (0.50 g, 0.81 mmol) was then added at once with vigorous stirring at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature for another 24 h. To imidize chemically, acetic anhydride (1 mL) and pyridine (1 mL) were added to the above mixture. The reaction mixture was dehydrated at ca. 125 °C for 6 h and then cooled to room temperature. The resulting polyimide was precipitated into methanol and collected by filtration. After being washed with methanol for 2 days in a Soxhlet extractor, the polymer was collected as a brown solid. The yield was 0.59 g (93.2%): *T*<sub>g</sub> 161 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 3.90 (br s, 4H, -NCH<sub>2</sub>-CH<sub>2</sub>O-), 4.02 (br s, 2H, -PhCH<sub>2</sub>Ph-), 4.36 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 6.89 (br s, 2H, Ar H), 6.98–7.38 (br m, 13H, Ar H), 7.49 (br m, 3H, Ar H), 7.75 (br m, 4H, Ar H), 8.13 (br s, 2H, Ar H). UV/vis (thin film on an ITO-covered glass): λ<sub>max</sub> = 438.7 nm. Anal. Calcd for C<sub>47</sub>H<sub>34</sub>N<sub>4</sub>O<sub>8</sub>: C, 72.10; H, 4.39; N, 7.16. Found: C, 71.78; H, 4.54; N, 7.12.

**Polymer PI-2-DANS.** To a 25 mL two-necked flask containing 4,4'-(hexafluoroisopropylidene)dianiline (0.27 g, 0.81 mmol) was added 3.5 mL of anhydrous NMP at 0 °C. After the diamine compound was dissolved completely, the dianhydride monomer 5 (0.50 g, 0.81 mmol) was added at once with vigorous stirring. The mixture was stirred at 0 °C for 2 h and at room temperature for another 24 h. PI-2-DANS was synthesized using a procedure similar to that for PI-1-DANS. Purification by Soxhlet extraction with methanol gave 0.68 g (91.9%) of a brown solid: *T*<sub>g</sub> 181 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 3.94 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 4.40 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>O-), 6.72–7.19 (br, 4H, Ar H), 7.19–7.63 (br, 14H, Ar H), 7.63–7.90 (br, 4H, Ar H), 8.14 (br, 2H, Ar H). UV/vis (thin film on Corning glass): λ<sub>max</sub> = 430.5 nm. Anal. Calcd for C<sub>49</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>F<sub>6</sub>: C, 64.05; H, 3.52; N, 6.10. Found: C, 64.20; H, 3.73; N, 6.08.

**Polymer PI-3-DANS.** To a 25 mL two-necked flask were added 4-bis(aminoethyl)amino-4'-nitrostilbene (0.26 g, 0.81 mmol) which was prepared as reported previously<sup>6</sup> and anhydrous NMP (4 mL). The solution was stirred at 0 °C until diamine dissolved completely and dianhydride 5 (0.50 g, 0.81 mmol) was then added at once with vigorous stirring at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature for another 24 h. The resulting polyimide was prepared as described. After the resultant was washed with methanol for 2 days in a Soxhlet extractor, 0.68 g (93.2%) of the polymer was collected as a brown solid: *T*<sub>g</sub> 168 °C. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, ppm): δ 3.62 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N(CO)<sub>2</sub>-), 3.76 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N(CO)<sub>2</sub>-), 3.97 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>-OAr-), 4.34 (br s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>OAr-), 6.77–7.05 (br, 6H, Ar H), 7.05–7.27 (br, 5H, Ar H), 7.27–7.44 (br, 4H, Ar H), 7.44–7.57 (br, 3H, Ar H), 7.57–7.75 (br, 5H, Ar H), 8.15 (br, 3H, Ar H). UV/vis (thin film on an ITO-covered glass): λ<sub>max</sub> = 437.5 nm. Anal. Calcd for C<sub>55</sub>H<sub>42</sub>N<sub>6</sub>O<sub>10</sub>: C, 68.55; H, 4.66; N, 9.23. Found: C, 68.71; H, 4.74; N, 8.71.

**Measurements.** <sup>1</sup>H NMR spectra were recorded on Bruker AM 200 and AM 300 spectrometers. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrometer and UV/vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. The melting points of the synthesized compounds were determined using a Fisher-Johns melting point apparatus. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere at a heating rate of 10 °C/min on a Dupont 2100 analyzer. The number- and weight-average molecular weights of polymers were estimated by gel perme-

ation chromatography (GPC) with polystyrene standards (columns Styragel HR5E4E2; solvent tetrahydrofuran). The refractive indices of the polymer film on a silicon wafer substrate were scanned through a full range from 500 to 1100 nm using a Woollam WVASE ellipsometer. Film thicknesses were determined using a instrument Tencor Alpha-Step 500 surface profilometer.

**Film Preparation and SHG Measurements.** PI-2-DANS showed remarkable solubility in DMF, NMP, cyclohexanone, and so forth. The best quality film was obtained from a 10% (by weight) polymer solution in cyclohexanone deposited on a Corning glass substrate. Prior to the film casting the polymer solution was filtered through a 0.45 μm Teflon membrane filter (Aldrich). The film was spin cast at room temperature at a rate ranging from 400 to 600 rpm. However, for PI-1-DANS and PI-3-DANS, turbid films were obtained after spin casting from their NMP solutions at the ambient temperature because of relatively low solubility. Heating both indium-tin oxide (ITO) covered glasses and the polymer solutions at ca. 100 °C for about 10 min before film casting increased the solubility and resulted in good optical quality films. The PI-1-DANS and PI-3-DANS films were spin cast at 1200 rpm from the 10% (by weight) NMP solutions. All films were dried for 6 h under reduced pressure at 120 °C to drive out residual solvent. These solvent-free films were used in the poling process using a high DC electric field. To further orient the dipole moments of the NLO chromophores, the films were poled in a corona-discharge setup. The poling was performed in a wire-to-plane geometry under in situ conditions. The discharging wire to plane distance was 1.0 cm and the temperature was gradually increased at a rate of 10 °C/min from room temperature to a temperature near the glass transition: PI-1-DANS, at 169 °C for 20 min, 5.0 kV; PI-2-DANS, at 185 °C for 30 min, 3.8 kV; PI-3-DANS, at 173 °C for 20 min, 5.0 kV. The samples were cooled to room temperature in the presence of the electric field. Finally, the poling field was removed. The PI-2-DANS film on an ITO-covered glass substrate developed turbidity during the poling process. An optically transparent film was obtained after the poling using a Corning glass as a substrate.

The second harmonic generation (SHG) experiments<sup>17,18</sup> were performed with a *p*-polarized beam at the fundamental frequency of a mode-locked Q-switched Nd:YAG laser (Lumonics HY750) operating at 10 Hz with 8 ns subpulses in each pulse train. The IR laser light passed through the attenuator, half wave plate, and polarizer was incident to the side of the film surface on the ITO glass. The second harmonic light from a sample was passed through a band-pass filter to remove a fundamental wave. The SHG signals from the *p*-polarizer were accumulated using a photomultiplier tube (Hamamatsu R-928) and averaged with a Boxcar averager (Stanford SRS250). The Maker Fringe pattern was obtained from measuring the SHG signal at 0.5° intervals using a rotation stage (Micro-control TL78). A 4.65 mm Y-cut quartz plate with a second-order nonlinearity of *d*<sub>11</sub> = 0.5 pm/V was used as a reference.

When a certain amount of absorption exists in the second harmonic region, a significant error in the effective SHG *d*-coefficient can occur. The effects of absorption have been considered to some extent for electric-field-induced SHG,<sup>19</sup> Maker fringes with wedges,<sup>20</sup> and poled polymer films.<sup>21</sup> Because our NLO polyimide sample films have small but nonnegligible absorption at 532 nm, this absorption must be considered in calculating the SHG coefficient of the films. The SHG coefficient of the film was calculated using the method developed by Herman et al. in which both the absorption and birefringence of the sample film as well as reflections were

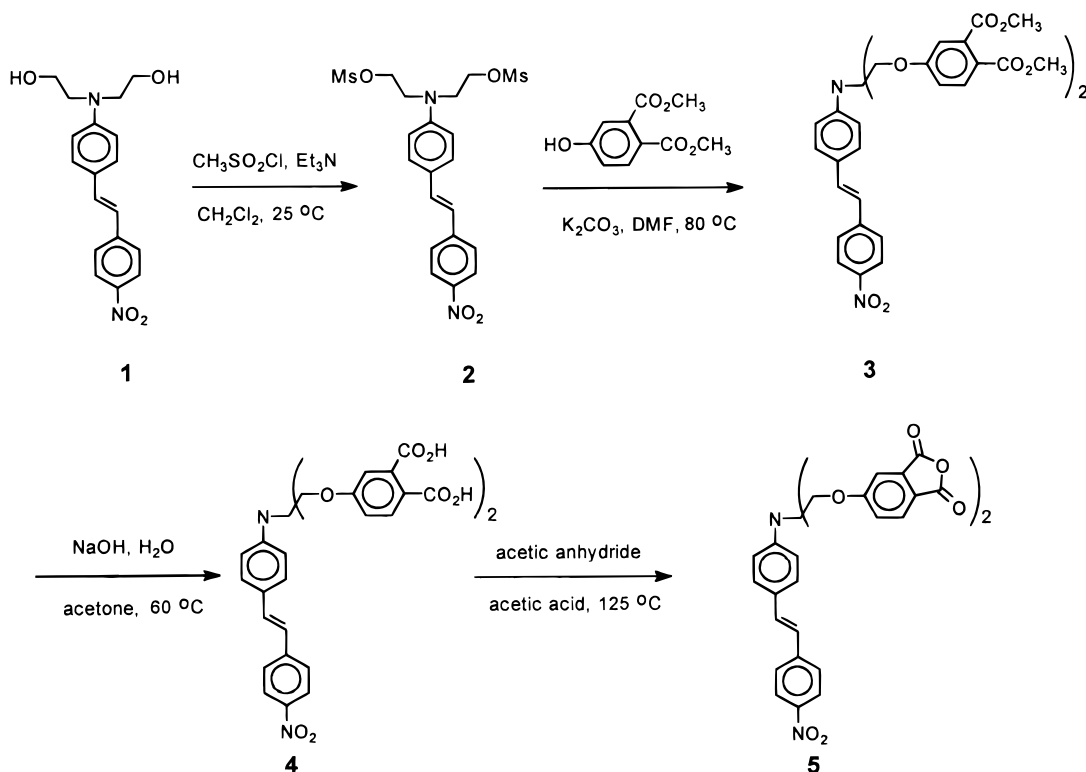
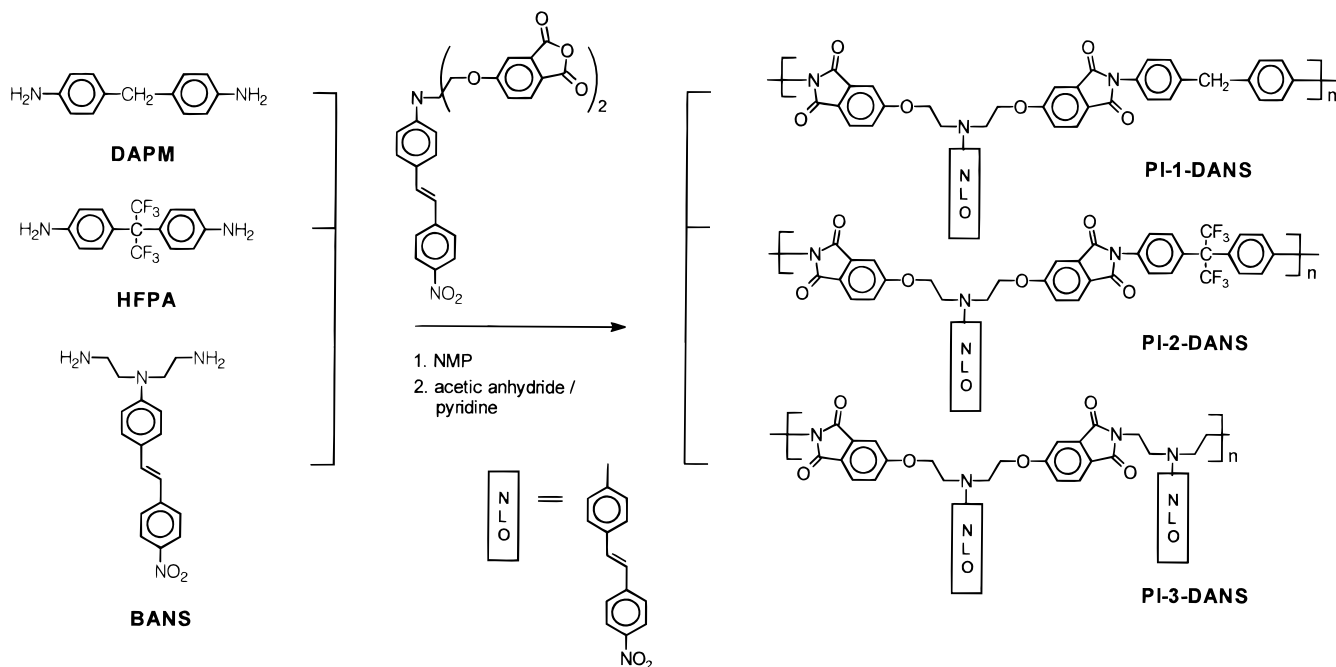
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**Scheme 1. Synthetic Route for the NLO Chromophore-Containing Dianhydride Monomer****Scheme 2. Synthetic Route for the Polyimides**

considered.<sup>22</sup>

## Results and Discussion

**Synthesis and Characterization.** The synthetic routes for the chromophore-containing dianhydride monomer and resulting polyimides are presented in Schemes 1 and 2. We incorporated 4-bis(hydroxyethyl)amino-4'-nitrostilbene **1**, which is widely used for the

second-order NLO material, into the polyimide backbone. Compound **1** was mesylated and followed by S<sub>N</sub>2 alkylation with 4-hydroxyphthalic acid dimethyl ester in DMF. Compound **3** is somewhat hygroscopic and must be maintained in a nitrogen atmosphere. Hydrolysis catalyzed by NaOH in a H<sub>2</sub>O/acetone cosolvent gave tetraacid **4** which was precipitated by adding the reaction solution dropwise to the aqueous HCl. Dehydration of compound **4** with acetic anhydride and acetic acid afforded the dianhydride monomer **5** containing the NLO chromophore. All intermediates, including the

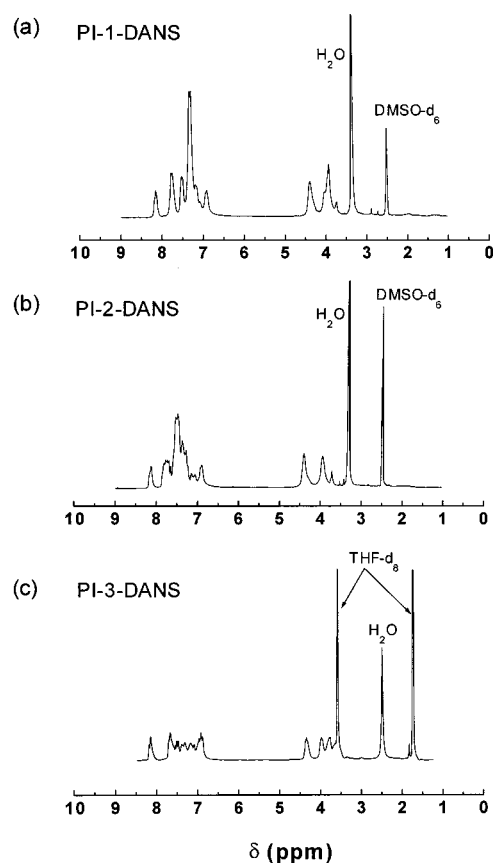
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monomer, were characterized by common spectroscopic techniques such as  $^1\text{H}$  NMR, IR, UV/vis, and elemental analysis and these results were in good agreement with the structures.

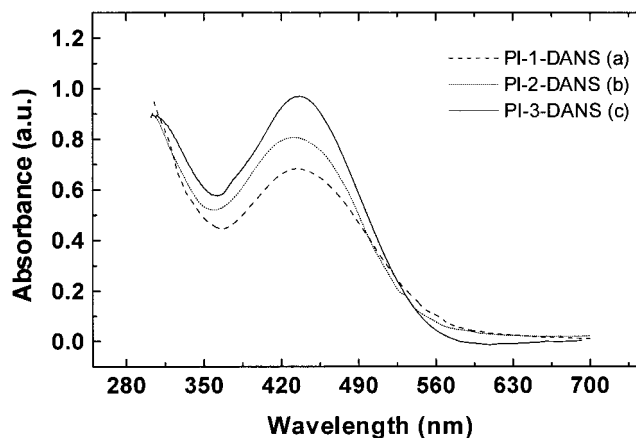
The present simple synthetic route may be applied to many kinds of NLO chromophores which have dihydroxy functional groups. The difficulty in the synthesis of chromophore-containing diamine compounds has limited the type of chromophores which may be incorporated into the polyimide backbone. Through this simple methodology, various chromophores can be incorporated into the polyimide backbone without requiring the synthesis of NLO-diamine compounds. To vary the physicochemical and optical properties of the polymers such as solubility, glass-transition temperatures, second-order optical nonlinearity, and so forth, three types of diamine compounds, DAPM, HFPA, and BANS, were used in the polymer synthesis.

The polymerization of diamines with the dianhydride monomer **5** is described in Scheme 2. Three types of polyimides, PI-1-, PI-2-, and PI-3-DANS, were prepared in anhydrous NMP by the condensation process followed by chemical imidization with acetic anhydride and pyridine. The resulting polymers were purified by Soxhlet extraction for 2 days using methanol as a solvent. These polyimides differ both in their main chain structure and chromophore content. The structures of PI-1-DANS and PI-2-DANS are similar, the former has a methylene group and the latter a hexafluoroisopropylidene group in the main chain, respectively. This small structural change results in considerable differences in physical and chemical properties of final polymers as described in detail in the following part. Both PI-1- and PI-2-DANS differ from PI-3-DANS in the chromophore content of the polymer backbone. In most NLO condensation polymers synthesized previously, only one of the monomers contained the NLO chromophore because of solubility of final polymers, synthetic difficulty, optical quality, and so forth. However, in the PI-3-DANS polymer, both monomers have NLO chromophores. There have been very few reports where the active functionalities are introduced into both comonomers.<sup>23,24</sup> This effectively produces double chromophore density relative to PI-1- and PI-2-DANS, and a much higher NLO activity can be anticipated. In addition, alkyl spacer groups and ether linkages make the polymers readily processible.

The number-average molecular weights,  $M_n$  of three polymers were 10 000 ( $M_w/M_n = 1.59$ ) for PI-1-DANS, 16 800 ( $M_w/M_n = 2.28$ ) for PI-2-DANS, and 11 800 ( $M_w/M_n = 2.13$ ) for PI-3-DANS, respectively. The polymers are readily soluble in aprotic polar solvents such as DMF, THF, NMP, and so forth. The  $^1\text{H}$  NMR spectra of three polymers (Figure 1) show signal broadening, but the chemical shifts are consistent with the proposed polymer structures. The assignments for these spectra were previously documented in the Experimental Section. The signal at 2.49 ppm originates from DMSO- $d_6$  and the broad peak at around 3.30 ppm comes from  $\text{H}_2\text{O}$  in the solvent. In the spectrum of PI-3-DANS, the lines at 1.73 and 3.58 ppm are assigned to the residual



**Figure 1.**  $^1\text{H}$  NMR spectra of (a) PI-1-DANS in DMSO- $d_6$ , (b) PI-2-DANS in DMSO- $d_6$ , and (c) PI-3-DANS in THF- $d_8$ .



**Figure 2.** UV/vis absorption spectra of three types of polyimides films.

hydrogens of THF- $d_8$ . The UV/vis absorption spectra of the polymers indicated absorption maxima at around 435 nm, due to the  $\pi-\pi^*$  transition of the stilbene-type chromophore (Figure 2). The IR spectra of the polymers were similar and confirmed the formation of imide group in all cases (Figure 3). The peaks at 1772 and 1719  $\text{cm}^{-1}$  are ascribed to the carbonyl groups in the imide linkages. Two strong absorption bands due to the nitro group in the NLO chromophore of the polyimides appeared at 1337 and 1516  $\text{cm}^{-1}$ . These results are consistent with the structures proposed, indicating that the NLO chromophore survived during the imidization process. In the PI-2-DANS case, the characteristic bands

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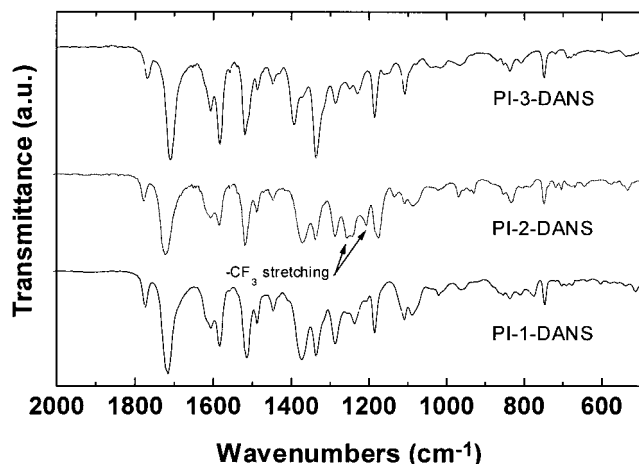


Figure 3. IR spectra of several polyimides with KBr pellets.

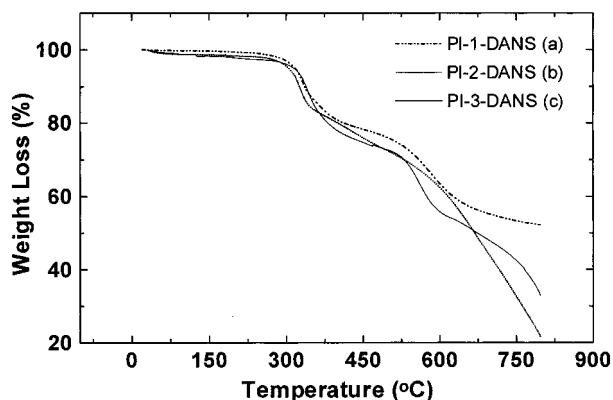


Figure 4. TGA thermograms of several polyimides (at a heating rate of 10 °C/min under nitrogen).

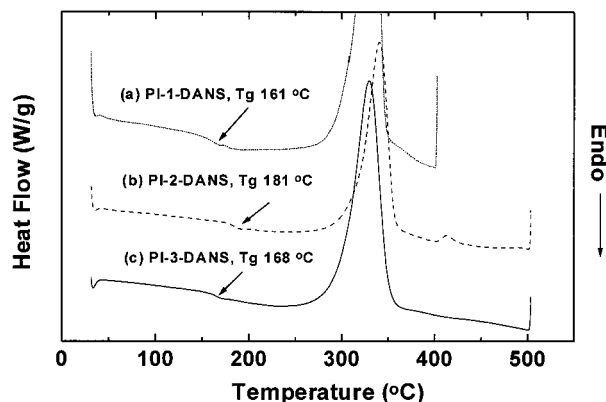


Figure 5. DSC thermograms of several polymers (at a heating rate of 10 °C/min under nitrogen).

at ca. 1260 and 1215  $\text{cm}^{-1}$  are due to  $-\text{CF}_3$  stretching in the polymer backbone.

In Figures 4 and 5, TGA and DSC thermograms of the polyimides are presented, respectively. It can be noticed that initial weight loss in the polymers begins at ca. 268–281 °C, which represents the onset of decomposition of the NLO-phore, and the breakdown of the polymer main chain occurs at around 455 °C. The DSC curves show a glass transition around 161 °C for PI-1-DANS, 181 °C for PI-2-DANS, and 168 °C for PI-3-DANS. These are relatively low values compared to those of common rigid polyimides and are attributed to flexibility in the polymer backbone containing ether linkages and the alkyl tether groups. The physicochem-

Table 1. Physicochemical Properties of the NLO Polyimides

polymers	$M_n$ ( $M_w/M_n$ ) <sup>a</sup>	$T_g$ (°C)	onset $T_d$ <sup>b</sup> (°C)	$\lambda_{\text{max}}$ (nm)
PI-1-DANS	10 000 (1.59)	161	272	438.7 (on ITO)
PI-2-DANS	16 800 (2.28)	181	281	430.5 (on Corning glass)
PI-3-DANS	11 800 (2.13)	168	268	437.5 (on ITO)

<sup>a</sup> Molecular weights of the final polymers were estimated by gel permeation chromatography using THF as an eluent. <sup>b</sup> The onset decomposition temperature from DSC.

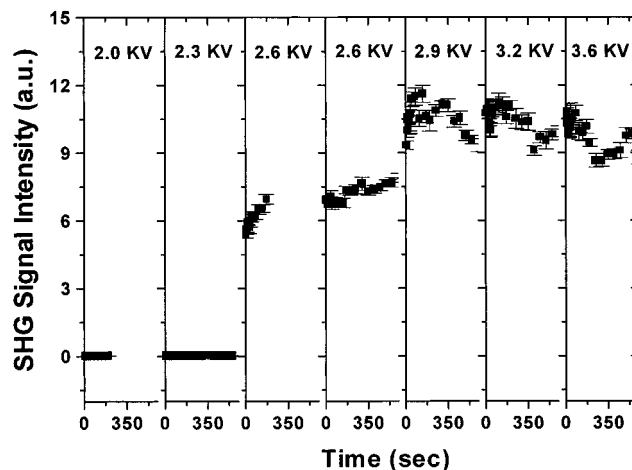
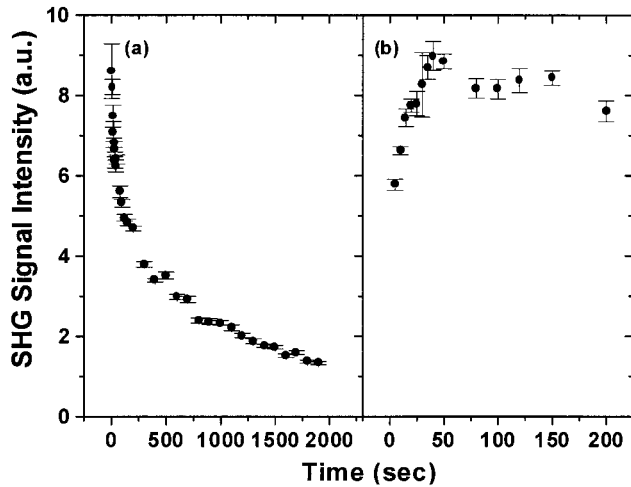


Figure 6. SHG signal dependence of PI-2-DANS upon the applied electric voltage at room temperature.

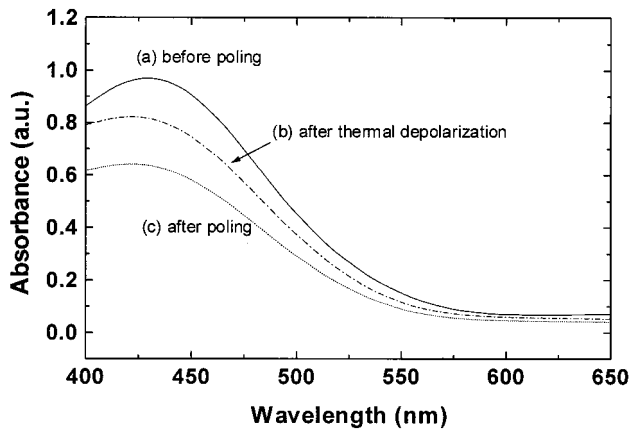
ical properties of these polymers are summarized in Table 1.

**Second-Order Optical Nonlinearity.** Some initial poling studies were performed to examine the performance of the polymers (i.e., optical nonlinearity and orientational stability of the aligned dipoles at elevated temperatures). The nonlinear optical characteristics were studied by the SHG method. In the case of PI-2-DANS, the best optical quality film was obtained by spin casting from 10 wt % cyclohexanone solution. To find the appropriate poling voltage, the SHG signal in thin films spin cast onto glass substrate was measured at ambient temperature. A corona wire to the slide glass distance of 1 cm was used. It was anticipated that no SHG signal be detected at room temperature based on the high  $T_g$  values for the polymers. However, the poling voltage dependence of the SHG signal shows that the dipole alignment occurs at room temperature at corona voltages above 2.6 kV (Figure 6). This is attributed to some rotation of the chromophores because of the free volume between the polymer chains and some contribution of the  $\chi^3$  effect. Similar room-temperature orientation of NLO chromophores in various polymer backbones has been reported by us.<sup>25</sup> However, this orientation disappeared rapidly within 10 min, after the electric field was removed (Figure 7a). This implies that although the chromophores can be oriented by the external electric field at room temperature, they revert to their original positions when the field is removed. When the electric field is on, the chromophores bonded to the main chain feel an orienting torque along the electric field. Since the chromophore is attached through the

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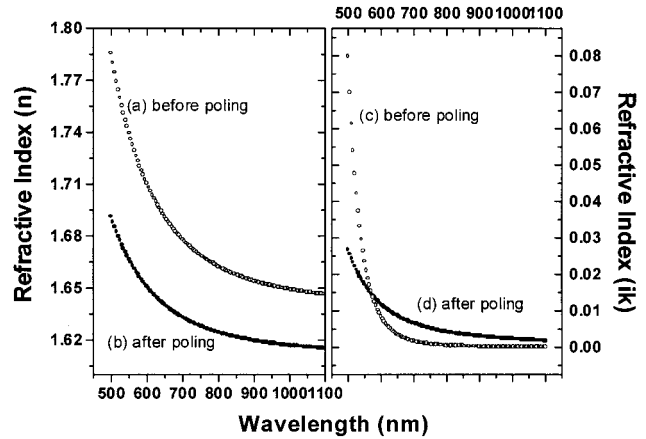
**Figure 7.** (a) Relaxation profile of aligned dipoles in PI-2-DANS after removing the electric field in the sample poled at ambient temperature. (b) Upon imposing the electric field again, the SHG signal was recovered to the initial value rapidly.



**Figure 8.** UV/vis absorption spectra of the PI-2-DANS films coated on the Corning glass substrates, (a) before poling, (b) after thermal depolarization, and (c) after poling.

main chain, this will in turn apply force to the main chain. As a result, the main chain will be elastically deformed. When the field is removed, dipoles return back to their original positions and the SHG signals rapidly decay to zero. In other words, a thermally stable arrangement may not be accomplished under ambient conditions. Upon imposing the electric field again to this randomly relaxed film, the SHG signal was rapidly recovered (Figure 7b).

In situ SHG measurement allows the monitoring of the nonlinear optical signal while the sample is being heated and poled. The in situ poling profile showed the increased alignment of the dipoles, as the temperature was raised to near the glass-transition temperature ( $T_g$ ). The films were poled at around  $T_g$  for about 30 min and cooled to room temperature and the electric field was removed. As shown in Figure 8, after the electric field poling, the transition moments of the NLO chromophores were aligned and the UV/vis spectra of PI-2-DANS exhibited a slight blue shift and a decrease in absorbance due to the induced birefringence. From the absorbance change, the order parameters of the poled films can be estimated. The estimated order parameter values were 0.38 for PI-1-DANS, 0.34 for PI-2-DANS,



**Figure 9.** Refractive indices of the PI-2-DANS films on a silicon wafer substrate before and after poling((a), (b) real part; (c), (d) imaginary part of the measured refractive index).

and 0.35 for PI-3-DANS, respectively. Figure 8b shows the recovered UV/vis absorption after undergoing thermal relaxation of the aligned dipoles. The reason for the incomplete recovery of the original absorbance may be due to partial degradation of the chromophores during the harsh poling process. In Figure 9, the in-plane refractive indices of poled and unpoled PI-2-DANS films coated on a silicon wafer substrates are presented. The refractive index values of the poled PI-2-DANS films are 1.6157 at 1064 nm and 1.6759 at 532 nm. The values of the poled film were reduced noticeably relative to those of the unpoled film. This may be caused by the poling-induced birefringence after the electric field poling. In addition, the absorption coefficient,  $\alpha_{2\omega}^f$  of the film at the second harmonic wavelength,  $\lambda$ , can be estimated from the imaginary part,  $ik$ , of the refractive index by the following equation:

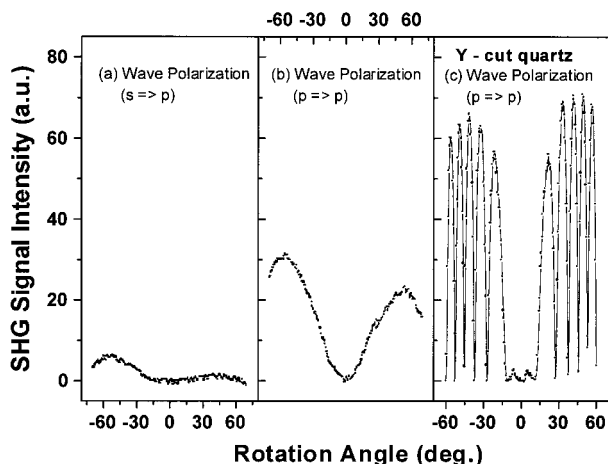
$$\alpha_{2\omega}^f = 4\pi\kappa_{2\omega}^f/\lambda$$

The estimated absorption at 532 nm with  $\kappa = 0.019$  (obtained from the imaginary part of the refractive index) was  $0.45 \mu\text{m}^{-1}$ , and that measured from UV/vis spectroscopy was  $0.328 \mu\text{m}^{-1}$ . It is thought that this discrepancy may come from the reflection losses at the air/film and film/substrate interfaces during the UV/vis absorption measurement. Studies of ultrathin films with thicknesses less than 100 nm required particular care, since the reflection losses at the air/film and film/substrate interfaces were comparable to the internal absorption losses of the films.<sup>26</sup>

Figure 10 shows the angular dependence of the SHG signals in the poled PI-2-DANS film. 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 light were directed to the samples and recorded (Figure 10a,b). The values of  $d_{31}$  and  $d_{33}$  for PI-2-DANS were 4.8 and 24 pm/V, respectively, using the fundamental wavelength of 1064 nm. In the isotropic model, the ratio of  $d_{33}/d_{31}$  is predicted to be about 3, which is in good agreement with published experimental data.<sup>27-31</sup> Our  $d_{33}/d_{31}$  value of

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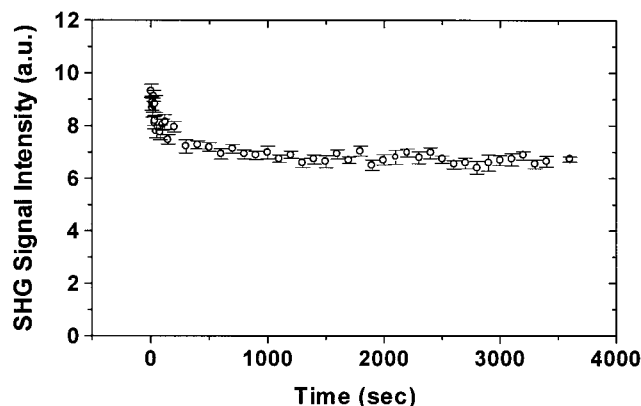
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**Figure 10.** Angular dependence of the SHG signals in a poled PI-2-DANS film compared with the signal of a Y-cut quartz plate.

5 indicates a substantial deviation from the isotropic behavior, which have also been observed elsewhere.<sup>32–34</sup> Such deviations can have a variety of origins, all rising from situations where one or more of the approximations made within this model are violated.<sup>35</sup> A typical situation includes poling at a high field strength,<sup>36</sup> strong interactions between the NLO-phores such as in liquid-crystalline phases,<sup>37</sup> or photophysical experiments carried out at optical frequencies near the resonance of the NLO-phore.<sup>38</sup> It has also been shown that higher ratios can arise if the mobility of the NLO-phores is significantly restricted by their immediate environment.<sup>32</sup> The deviation in  $d_{33}/d_{31}$  of the PI-2-DANS film may come from any or all of the reasons documented including ineffective poling.

After the complete poling cycle, the electric field was removed and the relaxation of the SHG signal was measured immediately over 1 h at room temperature. Figure 11 shows a typical temporal decay of the poling-induced nonlinearity and subsequent stabilization of the SH intensity at about 70% of the initial maximum value. As stated previously, the chromophores could be oriented at room temperature above the poling voltage of 2.6 kV, but randomized within 10 min after the electric field was removed (see Figure 7). This indicates that the stable conformation of the polymer chains may be

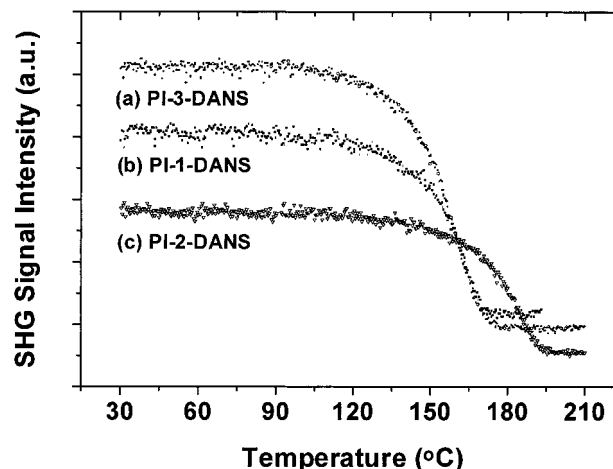


**Figure 11.** Relaxation profiles of aligned dipoles in PI-2-DANS right after removing the electric field at room temperature in a complete poling cycle.

**Table 2. Optical Properties of Various Polyimides**

polymers	chromophore content (wt %)	$\Phi^a$	$\alpha^b$ at 532 nm ( $\mu\text{m}^{-1}$ )	film thickness ( $\mu\text{m}$ ) <sup>c</sup>	$d_{33}$ (pm/V) ( $d_{33}/d_{31}$ ) <sup>d</sup>	$d_{33}(\infty)^e$ (pm/V)
PI-1-DANS	28.65	0.38	0.492	0.392	37 (3)	10
PI-2-DANS	24.41	0.34	0.328	0.430	24 (5)	7
PI-3-DANS	49.23	0.35	0.572	0.463	36 (3)	10

<sup>a</sup> Order parameters were calculated from UV/vis spectra before and after poling according to the following equation:  $\Phi = 1 - (A_p/A_0)$ .  $A_p$ : absorbance at  $\lambda_{\text{max}}$  after poling.  $A_0$ : absorbance at  $\lambda_{\text{max}}$  before poling. <sup>b</sup> Absorption coefficients at 532 nm after poling. <sup>c</sup> Film thickness was measured on the  $\alpha$  step surface profilometer. <sup>d</sup> In the case of PI-2-DANS, both  $d_{31}$  and  $d_{33}$  were measured using the Maker Fringe method, but the isotropic model approximation of  $d_{33} = 3d_{31}$  was used in cases of PI-1- and PI-3-DANS. <sup>e</sup> Non-resonant  $d_{33}$  values of these materials were obtained by using an approximate two-level model.<sup>39</sup>



**Figure 12.** Thermal stability of poling-induced alignments in (a) PI-3-DANS, (b) PI-1-DANS, and (c) PI-2-DANS.

accomplished above the glass-transition temperature, thereby stabilizing the dipole alignment. The SHG measurements, performed at a fundamental wavelength of 1064 nm, revealed large  $d_{33}$  values of 37 pm/V for PI-1-DANS and 36 pm/V for PI-3-DANS. Since the second harmonic wavelength is 532 nm, which is in the absorptive region of our polyimide samples, there is a certain amount of resonant enhancement in these  $d_{33}$  values. Since a longer wavelength laser source was not available to us, we calculated the nonresonant value of these materials by using the approximate two-level

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model.<sup>39</sup> It was found that the dispersion corrected  $d_{33}$  value was ca. 10 pm/V for PI-1-DANS, 7 pm/V for PI-2-DANS, and 10 pm/V for PI-3-DANS, respectively. The relatively low value for PI-3-DANS, even with twice the chromophore density, may come from the ineffective poling because of the matrix rigidity and some aggregation that occurred between the NLO chromophores. These optical properties of the polymers are summarized in Table 2.

To evaluate the orientational stability of these polymers, the real time NLO decay of the SHG signal in poled polymer films as a function of temperature was investigated (Figure 12). The temperature was increased at a rate of 5 °C/min from 30 °C to above 200 °C. As the temperature increased, the rate of decay in the SHG signal increased because of a faster relaxation of the dipole orientation. In all cases, the initial SHG signal was maintained up to ca. 125 °C without any measurable decay. In PI-1- and PI-3-DANS, decay onset occurs around 130 °C and the SHG signal reaches zero at around 175 °C. However PI-2-DANS showed remarkable thermal stability of the dipole alignment until ca. 170 °C without any detectable decay. PI-2-DANS also exhibited the highest glass transition and thus the most stable orientation. These results indicate that these materials may be useful for practical applications. Especially PI-2-DANS may be the most promising

candidate based on its processibility and stability. Because of good processibility and orientational stability of the final polyimides, it is anticipated that many device elements can be fabricated.

### Conclusions

Three functionalized NLO polyimides were prepared through a new alternate synthetic route in which an NLO chromophore was incorporated into a dianhydride monomer. They showed high second-order optically nonlinear activity and good thermal stability of the aligned dipoles. The resonance enhanced  $d_{33}$  values ranged between 24 and 37 pm/V. The SHG signal was stable up to ca. 125 °C. In particular, PI-2-DANS showed a remarkable thermal stability without any measurable decay until about 170 °C. The synthetic route proposed may be applied to various NLO chromophores, and because of the versatility of the reaction scheme, many new materials can be expected.

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