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# Facile synthesis of new NLO-functionalized polyimides *via* Mitsunobu reaction

**Chong-Bok Yoon and Hong-Ku Shim***

*Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, 305-701 Korea. E-mail: hkshim@sorak.kaist.ac.kr, Tel: 82-42-869-2827, Fax: 82-42-869-2810*

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Three polyimides containing a nonlinear optical (NLO) chromophore were prepared through a new synthetic pathway. Coupling of dihydroxy and diimide compounds yielded the polyimide. Due to the mild conditions of polymerization, a chemically labile hemicyanine dye could be incorporated in the polyimide backbone successfully. The molecular weights of the polyimides obtained ranged from 8200 to 14 400, and the glass transitions occurred between 135 °C and 198 °C. The second-order NLO properties were characterized by using the second harmonic generation (SHG) technique. The second-order NLO coefficients ($\chi^{(2)}$) of the polyimides were 82 pm $V^{-1}$ and 122 pm $V^{-1}$ with reference to quartz crystal, and the nonlinearity of those polymers was stable at 100 °C without large loss.

## Introduction

Nonlinear optical (NLO) phenomena have been researched extensively for a number of years for future photonic technology.[1,2] Classically, inorganic crystals such as lithium niobate ($LiNbO_3$) have been used as materials for NLO devices. The cost and processability problem, however, have led to the development of organic polymers as materials for NLO devices. Many NLO-functionalized polymers have been synthesized because of their several advantages over their inorganic counterparts.[3,4] However several problems limited the applicability of organic polymers as materials for NLO devices, such as low NLO activity and poor temporal stability at high temperature. To solve these problems, several methods have been tried. Synthesis of a functionalized polymer with a highly NLO-active chromophore covalently attached to the rigid polymer backbone has been a typical approach, but other systems such as thermal or photo-crosslinkable network polymers, main chain polymers, and guest–host systems have been reported.[5–8] Among those, polyimide systems with high glass transition temperatures ($T_g$) were extensively considered due to their advantages such as higher temperature stability, lower optical loss and better mechanical properties.[9–13] The methods that were reported for the synthesis of NLO-functionalized polyimides include the polymerization of polyamic acid precursors and imidization to give the cyclic imide structure. These methods, however, include a difficult procedure for the synthesis of the chromophore-containing diamine monomers.[9,10] Furthermore, the fact that few chromophores can survive under the relatively harsh chemical conditions of the monomer synthesis and the imidization of the polymer severely limits the application of the methodologies.

We have devised a facile approach for the synthesis of NLO-functionalized polyimides.[14] This is a direct preparation of polyimide from diimide monomer and dihydroxy monomer through the Mitsunobu condensation.[15] By performing direct polymerization into polyimides under the mild Mitsunobu conditions, the harsh imidization process of the polyamic acid can be avoided and the synthesis of chromophore-containing diamine monomers is also unnecessary. Therefore, a chromophore with large first-order hyperpolarizability could be incorporated in the polyimide backbone without decomposition of the chromophore molecules. We chose hemicyanine dye as the NLO component since it has an extraordinarily high $\beta$ value compared with other NLO chromophores.[16] We have reported several polymer systems containing this moiety.[17,18] However, the difficulty in synthesizing the chromophore-containing diamine monomer and the instability in the high temperature range have prevented the introduction of the hemicyanine moiety to polyimide systems. In this paper, we discuss the synthesis of three polyimides containing NLO chromophores and the results of second-order NLO properties of the polymers.

## Experimental

### Materials

*N*,*N*-Bis(2-hydroxyethyl)aniline and phosphorus oxychloride were purchased from TCI Inc. 4-Nitrobenzyl bromide, triethyl phosphite, hexafluoroisopropylidenediphthalic anhydride, urea, diethyl azodicarboxylate, triphenylphosphine were purchased from Aldrich Co. Tetrahydrofuran, methylene dichloride, methanol, acetic acid, hydrogen bromide, benzoyl chloride were purchased from Junsei Co. All materials and solvents were used as received. *N*,*N*-Dimethylformamide was distilled under reduced pressure over anhydrous phosphorus pentoxide. For Soxhlet extraction, cellulose extraction thimbles from Whatman Co. (Cat. No. 2800260) were used.

### Monomer synthesis

***N*,*N*-Bis(2-benzoyloxyethyl)aniline (1).** To a mixture of 7.20 g (47.8 mmol) of *N*-(2-hydroxyethyl)-*N*-methylaniline and 8.1 g (57.3 mmol) of benzoyl chloride in 100 mL of methylene chloride was added 5.8 g (57.3 mmol) of triethylamine, and the resulting mixture was stirred at room temperature. After 1 day, the reaction mixture was cooled and extracted with methylene chloride. The organic layer was washed with water and then was dried with anhydrous magnesium sulfate. A white solid was obtained by evaporation of the solvent and further recrystallized with methanol. The yield was 18.4 g (97%). $M_w(C_{24}H_{23}NO_4) = 389.43$, mp 80.2 °C; $^1$H-NMR ($CDCl_3$) $\delta$ 7.99 (d, ArH, 4H), 7.54–7.21 (m, ArH, 8H), 6.88 (d, ArH, 2H), 6.74 (t, ArH, 1H), 4.51 (t, N-$CH_2$*$CH_2$*OH, 4H), 3.82 (t, N-*$CH_2$*$CH_2$OH, 4H).

**4-[*N*,*N*-Bis(2-benzoyloxyethyl)amino]benzaldehyde (2).** In a flask was placed 50 mL of anhydrous dimethylformamide while the flask was cooled in an ice bath. Then 8.4 g (55 mmol) of phosphorus oxychloride was added dropwise with stirring. After 30 min, 18.3 g (47 mmol) of compound **1** was added to the flask. The solution was heated at 60 °C for 2 hours. The reaction mixture was then cooled and poured over crushed ice in a beaker, and neutralized to pH 6–8 by dropwise addition of saturated sodium acetate solution. The mixture was extracted with ethyl acetate. The extracts were washed with water, dried with magnesium sulfate, and then concentrated. The resulting white solid was further purified by crystallization with methanol to yield 13.5 g (69%) of product. $M_w(C_{25}H_{23}NO_5)=417.44$, mp 82.5 °C; $^1$H-NMR ($CDCl_3$) $\delta$ 9.74 (s, –CHO, 1H), 7.96 (d, ArH, 4H), 7.74 (d, ArH, 2H), 7.54–7.36 (m, ArH, 4H), 6.92 (d, ArH, 2H), 4.54 (t, $NCH_2C\mathit{H}_2OH$, 2H), 3.90 (t, $NC\mathit{H}_2CH_2OH$, 2H).

**4-[Bis(hydroxyethyl)amino]-4′-nitrostilbene (3).** 12.0 g (28.7 mmol) of compound **2** and 8.50 g (28.7 mmol) of diethyl 4-nitrobenzylphosphonate were dissolved in 200 mL of anhydrous tetrahydrofuran and then sodium hydride 1.5 g (30 mmol) was added to this solution. The mixture was stirred at room temperature for 30 minutes, and then was refluxed at 80 °C for a further 8 hours. The reaction mixture was cooled to room temperature and 100 mL of methanol was added to the solution which was then kept at ambient temperature for 3 hours. After evaporation of the solvents, the resulting red precipitate was collected by filtration. The red precipitate was purified by recrystallization from methanol to give a red solid. The yield was 5.4 g (57%); mp 182–184 °C. Calc. for $C_{18}H_{20}N_2O_4$: C, 66.3; H, 5.6; N, 8.6%. Found: C, 66.3; H, 5.7; N, 8.7%. $^1$H-NMR (DMSO-$d_6$) $\delta$ 8.16 (d, ArH, 2H), 7.72 (d, ArH, 2H), 7.42 (d, ArH, 2H), 7.35 (d,–CH=CH–, 1H), 7.10 (d, –CH=CH–, 1H), 6.70 (d, ArH, 2H), 4.76 (t, $CH_2O\mathit{H}$, 2H), 3.56–3.45 (m, $NC\mathit{H}_2C\mathit{H}_2OH$, 8H).

**(*E*)-*N*-Butyl-4-[2-[4-bis(2-hydroxyethyl)aminophenyl]ethenyl]-pyridinium tetraphenylborate (4).** The monomer was prepared by the previously reported method.[14]

**5-[1-(1,3-Dioxoisoindolin-5-yl)-2,2,2-trifluoro-1-(trifluoromethyl) ethyl]isoindoline-1,3-dione (5).** 5.0 g (11.3 mmol) of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (HDPA) was reacted with 1.38 g (22.6 mmol) of urea at 200 °C for 1 hour without solvent and then cooled to room temperature. The purified diimide was obtained by washing the reaction mixture with water. The yield is 4.75 g (90.1%); mp 285–288 °C. Calc. for $C_{19}H_8N_2O_4F_6$: C, 51.6; H, 1.8; N, 6.3%. Found: C, 51.6; H, 1.7; N, 6.3%. $^1$H NMR (DMSO-$d_6$) $\delta$ 11.6 (s, –NH, 2H), 7.96 (d, ArH, 2H), 7.79 (d, ArH, 2H), 7.63 (s, ArH, 2H).

**2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane (6).** *N*,*N*′-Dimethyl-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane diimide (16.5 g, 37.3 mmol) was dissolved in 70 mL of acetic acid and 70 mL of concentrated aqueous hydrobromic acid was added to the mixture. The mixture was hydrolyzed at 125 °C for 24 hours and then cooled to room temperature. The white precipitate was filtered and thoroughly dried under reduced pressure. The yield is 13.2 g (63.6%). $M_w(C_{31}H_{24}O_{10})=556.53$, mp 126–128 °C; $^1$H-NMR (DMSO-$d_6$) $\delta$ 14.5–12.5 (br s, –COOH 4H), 7.75 (d, ArH, 2H), 7.30 (d, ArH, 4H), 7.08 (m, ArH, 8H), 1.67 (s, C–$CH_3$, 6H).

**2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (7).** 7.0 g (12.6 mmol) of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane was dissolved in 150 mL of acetic acid and 20 mL of acetic anhydride was added to the mixture. The mixture was dehydrated at 125 °C for 4 hours and then cooled to room temperature. The white precipitate was filtered and thoroughly dried under reduced pressure. 5.37 g of product was obtained (yield = 82.2%). $M_w(C_{31}H_{20}O_8)=520.49$, mp 177 °C; $^1$H-NMR ($CDCl_3$) $\delta$ 7.92 (d, ArH, 2H), 7.43 (two d, ArH, 2H), 7.34 (m, ArH, 6H), 7.03 (d, ArH, 4H), 1.74 (s, C–$CH_3$, 6H).

**2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane diimide (8).** The neat mixture of the anhydride **2** (2.18 g, 4.19 mmol) and urea (0.25 g, 41.6 mmol) was reacted at 200 °C for 2 hours and then cooled to room temperature. The solid was ground into a fine powder and further reacted at 200 °C for 1 hour and cooled to room temperature. The powder produced was washed with distilled water several times and dried thoroughly. 1.95 g of product was obtained (yield = 89.8%); mp 252–254 °C. Calc. for $C_{31}H_{22}N_2O_6$: C, 71.8; H, 4.3; N, 5.4%. Found: C, 71.7; H, 4.1; N, 5.3%. $^1$H-NMR (DMSO-$d_6$) $\delta$ 11.27 (br s, 2H), 7.78 (d, 2H), 7.33 (m, 6H), 7.18 (s, 2H), 7.07 (d, 4H), 1.68 (br s, 6H).

### Preparation of sample for determining NLO properties

The polymer solution was filtered through a 0.45 μm Teflon filter and spin cast to the precleaned (with isopropyl alcohol, acetone) indium-tin oxide (ITO) coated glass substrate to give a film whose thickness was around 1 μm. The films obtained were submitted to the vacuum oven to remove residual solvent. After drying the polymer samples, the corona-poling was performed at increasing temperature. The corona discharge was generated with a tungsten wire of thickness 20 μm.

### Analyses and spectroscopic measurements

$^1$H-NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrophotometer and UV–visible spectra were measured on a Shimadzu UV-3100S with wavelengths between 300 and 700 nm. Thermogravimetric analyses (TGA) were performed with a Dupont 9900 analyzer under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer DSC-7 with a heating rate of 10 °C min$^{-1}$. The second-order nonlinearity of these polymer samples was measured by second harmonic generation (SHG) methods using 1064 nm laser radiation. A polarized *Q*-switched Nd : YAG laser with an 8 ns pulse width and a 10 Hz repetition rate was used as the light source. The second harmonic signal was detected by a photomultiplier tube and averaged over 300 pulses in a boxcar integrator.

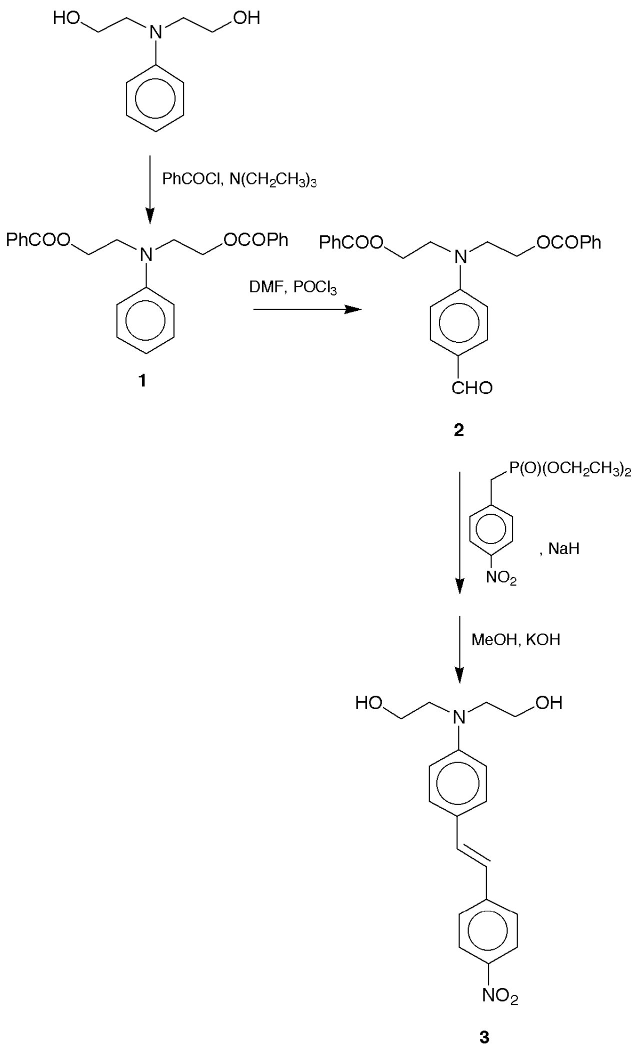
### Calculating SHG coefficient by Maker fringe method

Previously we calculated the second-order SHG coefficient ($\chi^{(2)}$) in the way reported by Jerphagnon and Kurtz.[19] However the absorption loss could not be ignored in the calculation of $\chi^{(2)}$ values. As PI1 and PI3 have significant absorption at 532 nm, we should consider the absorbed loss of second-harmonic generated light. The model used in the calculation of $\chi^{(2)}$ values was reported by Herman *et al.*[20]

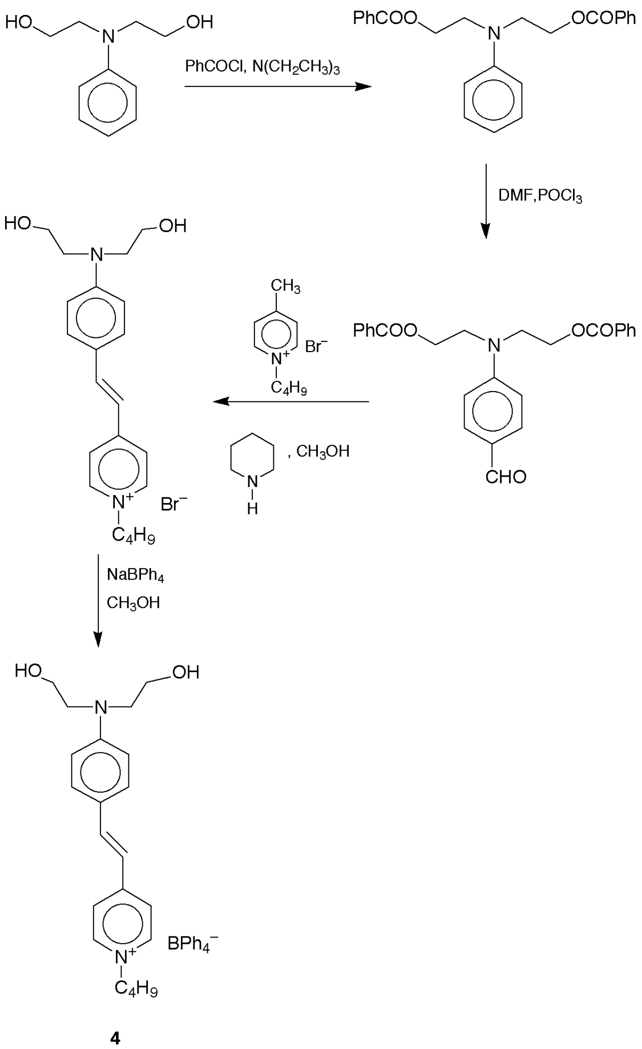
## Results and discussion

### Synthesis of polyimide

The synthetic procedures for monomers and polymers are shown in Schemes 1–4. In general, polyimides have a rigid structure and show poor solubility in common solvents. For better solubility of the final polyimide, two monomeric diimide compounds were prepared from 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BEA) which is well known as the monomer for ULTEM™ and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (HDPA). The synthesis of the diimide monomer from the dianhydride is a one-pot imidization of HDPA using urea as the nitrogen source. The



**Scheme 1** Synthetic route to compound **3**.



**Scheme 2** Synthetic route to compound **4**.

anhydride compounds were reacted with urea at 200 °C for 1 hour to give nucleophilic substitution of nitrogen into the anhydride moiety. After the completion of the reaction, the peaks corresponding to the imide protons were observed at 11.3 and 11.6 ppm in the $^1$H-NMR spectrum. The dihydroxy monomer containing hemicyanine dye was synthesized by a method previously reported by us.[14] The polymerization reaction between the diimide and dihydroxy monomers was executed by Mitsunobu reaction using diethyl azodicarboxylate (DEAD) and triphenylphosphine in anhydrous tetrahydrofuran (THF) solvent. Fig. 1 shows the $^1$H-NMR spectra of the monomeric compounds (**3**, **5**) and PI1. After polymerization, the peak at 11.6 ppm which corresponds to the imide proton of the monomer disappeared in the final polymer completely, indicating the reaction between diimide and dihydroxy monomer. In the case of PI2 and PI3 which contain the hemicyanine moiety, a similar trend was observed. The Soxhlet extraction with methanol was executed for two days to purify the resulting polyimides. The molecular weights of the purified polyimides (Table 1), determined by gel permeation chromatography (GPC) with a polystyrene standard, ranged from 8200–14 400 for weight averaged molecular weight ($M_w$). PI2 and PI3 showed lower molecular weights than PI1. The bulkiness and ionic character of the tetraphenylborate anion should have retarded the Mitsunobu reaction to give a shorter polymer chain.

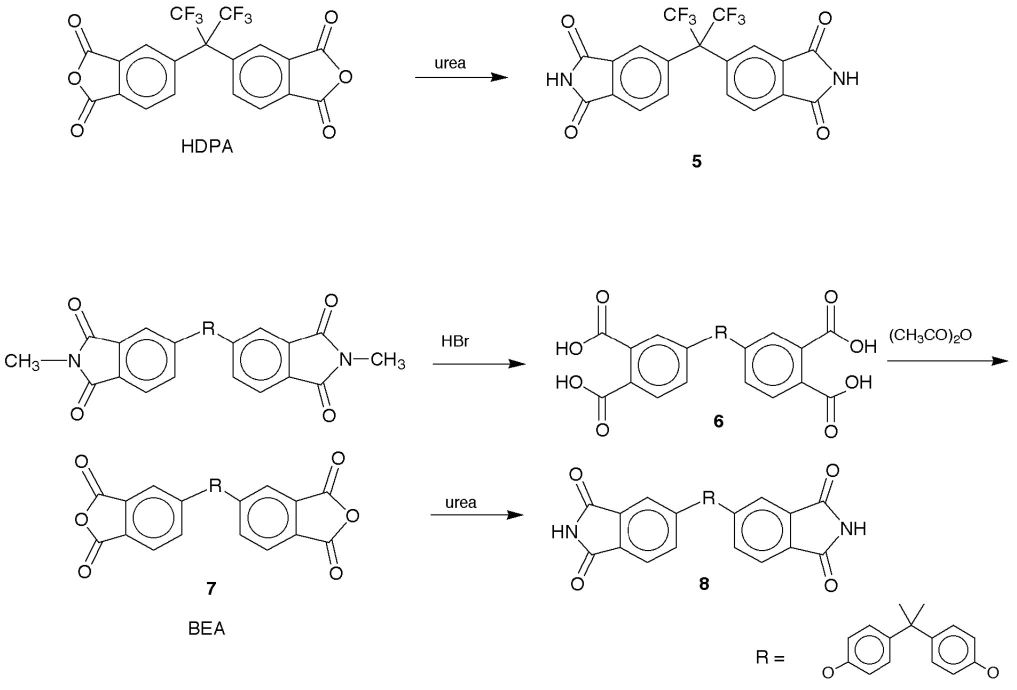
### Optical and basic properties of the polyimides

These polymers were readily soluble in THF, cyclohexanone, *etc.* From cyclohexanone solutions of PI1, PI2 and PI3, good optical quality thin films can be prepared onto glass substrates by spin coating. The polymer structures were characterized by UV–visible absorption and FT-IR spectroscopy. FT-IR spectra of the polyimides (PI1) showed the characteristic absorption peak at 1720 cm$^{-1}$ attributed to the imide rings, which does not appear in the spectrum of the dihydroxy monomer (**3**) (Fig. 2).[21] Other polyimides (PI2 and PI3) showed similar peaks at 1720 cm$^{-1}$. In the UV absorption spectra, the PI1 showed an absorption maximum at 432 nm corresponding to the dialkylaminonitrostilbene (DANS) moiety (Fig. 3). PI2 and PI3 also showed similar characteristics of hemicyanine dye

**Table 1** The properties of three NLO polyimides

| Polymer | $M_w$ (PDI) | $T_g$/°C[a] | $T_d$/°C[a] | α/cm$^{-1}$[b] | $\chi^{(2)}_{33}$/pm V$^{-1}$ | $\lambda_{max}$/nm | $\chi^{(2)}_{33}(0)$/pm V$^{-1}$[c] |
|---|---|---|---|---|---|---|---|
| PI1 | 14,397 (1.87) | 198 | 332 | $3.3 \times 10^2$ | 82 | 432 | 26 |
| PI2 | 10,780 (1.48) | 135 | 226 | $8.1 \times 10^2$ | — | 467 | — |
| PI3 | 8228 (1.89) | 175 | 227 | $8.2 \times 10^2$ | 122 | 467 | 24 |

[a] The temperature where weight remained up to 95%. [b] Absorption constant. [c] $\chi^{(2)}_{33}(0)$ is measured using the two-level model.



**Scheme 3** Synthetic route to diimide monomers **5** and **8**.

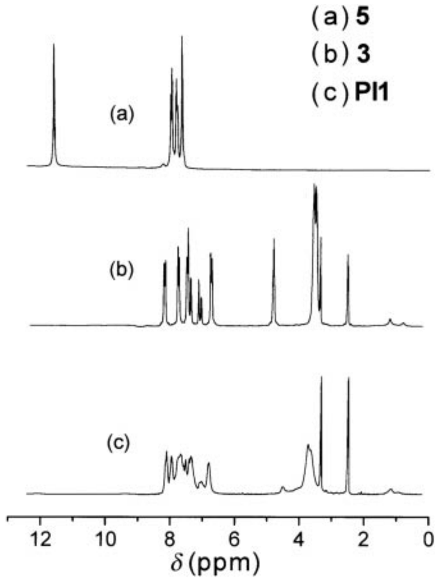


**Fig. 1** $^1$H NMR spectra of **3**, **5** and PI1.

that gave maximum absorption at 467 nm. There was no detectable change of UV absorption in PI2 and PI3 which indicated that the chain polarities of the polymer backbones of PI2 and PI3 were not significantly different.

Thermal properties of the polyimides were examined by TGA and DSC measurements. In the TGA thermograms of polyimides (Fig. 4), the thermal stabilities of the polymers were observed. Since the polyimide chain maintained its stability above 500 °C,[18] the weight losses should be the sole result of the chromophore decomposition. We defined $T_d$ as the temperature where the weight of polymer remained up to 95%. In Table 1, the $T_d$ of PI1 was 332 °C, similar to results obtained with NLO-functionalized polyimides prepared by other methods. The $T_d$ of PI2 and PI3, however, were around 226 °C and showed relatively poor thermal stability. The instability of PI2 and PI3 is attributed to the hemicyanine moiety with a bulky tetraphenylborate anion. This suggestion is supported by the fact that the observed weight loss corresponds with the fraction of the tetraphenylborate moiety in the overall molecular weight of the repeating unit. The molar weight of the repeating unit of PI3 was 1062.9 and that of the tetraphenylborate anion 319.2, giving the weight fraction of the tetraphenylborate anion to the polyimide repeating unit of about 30%, a value identical to the weight loss of PI3 at 300 °C. The $T_g$ of PI3 (175 °C) was higher than that of

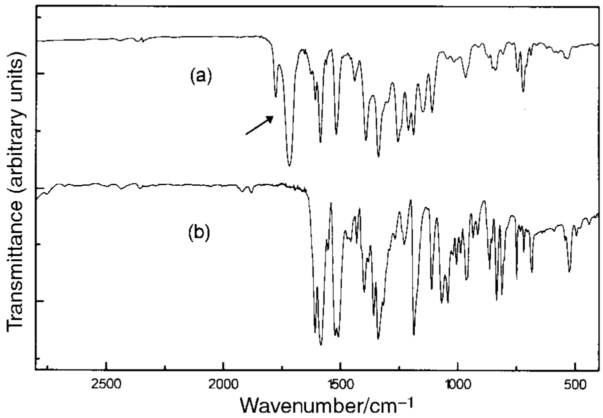


**Fig. 2** FT-IR spectra of (a) PI1 and (b) dihydroxy monomer **3**.

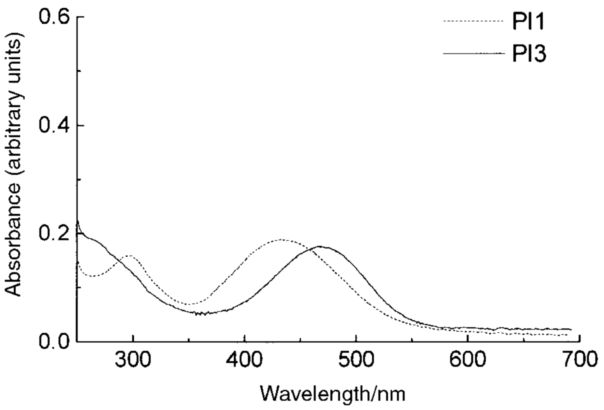
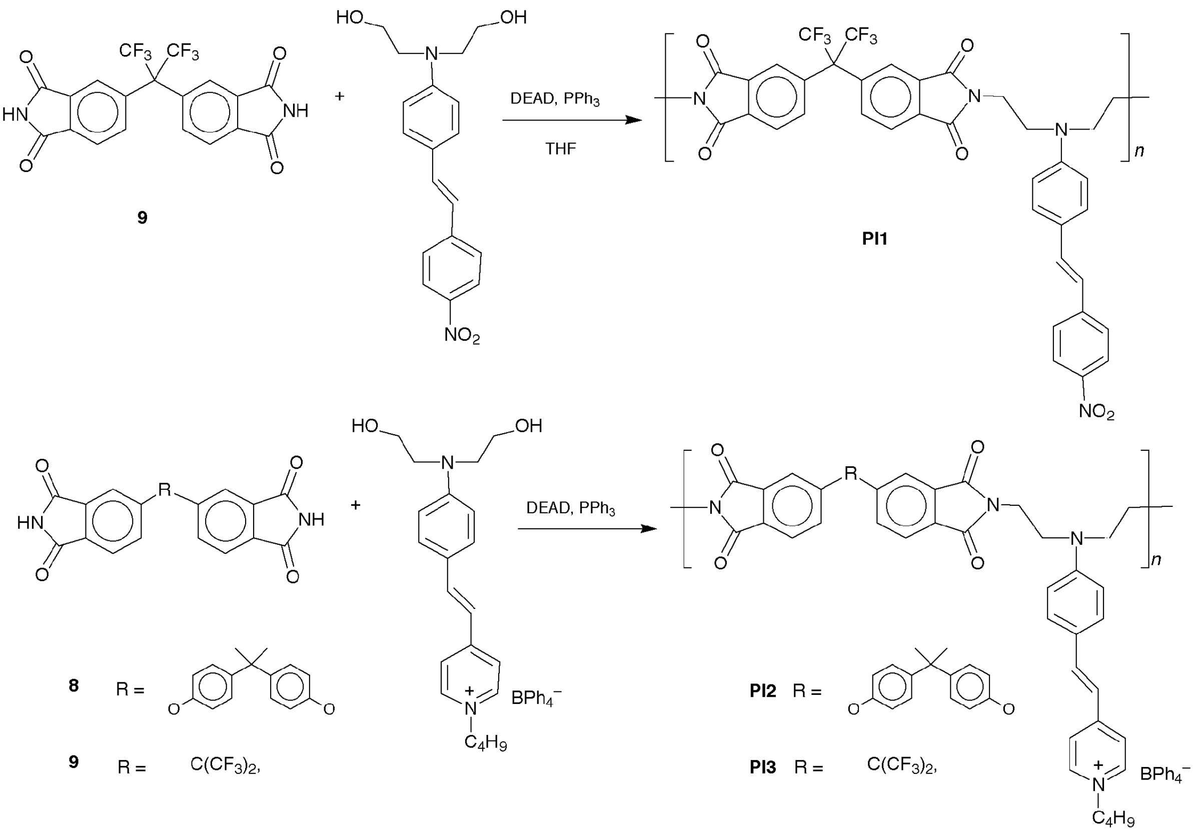


**Fig. 3** UV–visible absorption spectra of polymer films of PI1, PI3.



**Scheme 4** Synthetic pathway for PI1, PI2 and PI3.

PI2 (135 °C). It was thought that the more flexible units (bisphenol A unit) of PI2 lowered the $T_g$. In the comparison of PI1 and PI3, PI1 showed higher $T_g$ than PI3, which may be due to the effect of the difference in chromophores. The bulkier hemicyanine dye should have lowered the crystallinity to yield the glass transition at lower temperature.

### Sample preparation and measurement of second-order NLO properties

The second-order NLO process requires that the material must be noncentrosymmetric. For the amorphous polyimide films, the centrosymmetry can be broken by corona-discharge poling when the film is heated up to the $T_g$ so that the molecular dipole can be oriented.[5,22] PI1 and PI3 were dissolved in cyclohexanone and cast onto indium-tin oxide (ITO) layers to form thin films of 1–3 μm. Because the decomposition temperatures of the polyimides were higher than the $T_g$ of these polymers, we performed the poling step at a slightly higher temperature than the $T_g$ of each polymer holding the electric field under the nitrogen flow. Tungsten wire of 20 μm thickness was used to generate the corona charge. The second-order nonlinearity of polymer samples (PI1, PI3) was measured using a second harmonic generation (SHG) method at 1064 nm as the fundamental wavelength. The $\chi^{(2)}{}_{33}$ values of PI1 and PI3 measured using the angular dependence method with a quartz crystal as the reference[20] were found to be 82 and 122 pm V$^{-1}$, respectively (Fig. 5). PI3, which contained the hemicyanine dye, showed a larger $\chi^{(2)}{}_{33}$ value than that of PI1 containing a DANS moiety. However, the resonance effect on SHG measurement should not be ignored in real device applications. We calculated nonresonant values by a two-level model.[23] As the hemicyanine dye showed maximum absorption at longer wavelength, the $\chi^{(2)}{}_{33}(0)$ values of PI1 became similar to those of PI3. We thought this similarity was the result of the bulkiness of the hemicyanine moiety. In general, $\chi^{(2)}$ values can be specified as eqn. (1)[5]

$$\chi^{(2)} \propto \frac{N^2\mu\beta}{V(N)} \tag{1}$$

where $N$ is number of NLO chromophores; $\mu$, dipole moment; $\beta$, first-order hyperpolarizability; $V(N)$, specific volume of NLO chromophore. Although the hemicyanine dye has a larger $\beta$ value than DANS and thus gives increased $\chi^{(2)}$ values, its bulkiness lowers the chromophore density ($N/V$) in the polymer films resulting in smaller $\chi^{(2)}{}_{33}(0)$ values.

Because the thermal relaxation of dipole orientation is related to the free volume which is linked to the glass transition temperature, the thermal stability of the NLO properties of the poled polymers can be predicted from the $T_g$ of each polymer. At room temperature, all polyimides were significantly stable and there was no decay in the intensity of the SHG signal. All polymers sustained their nonlinearity at 100 °C in air for several hundred hours. Because the observation of temporal stability is a time-consuming experiment, we performed the temperature-dependent SHG measurement. Fig. 6 shows the dynamic thermal stabilities of PI1 and PI3. PI1 and PI3

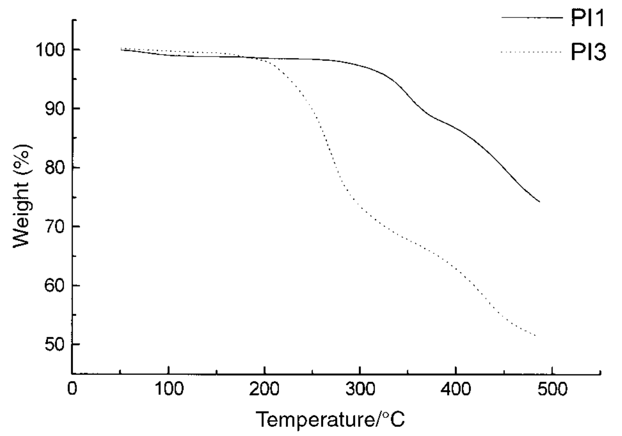


**Fig. 4** Thermogravimetric analysis (TGA) of PI1 and PI3.

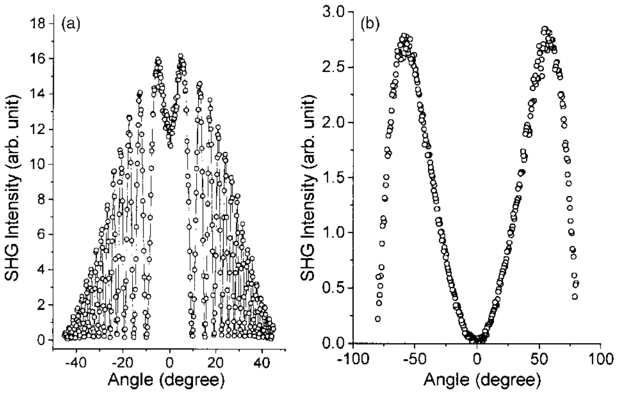


**Fig. 5** Maker fringe pattern of (a) quartz crystal (Y-cut) and (b) PI1.

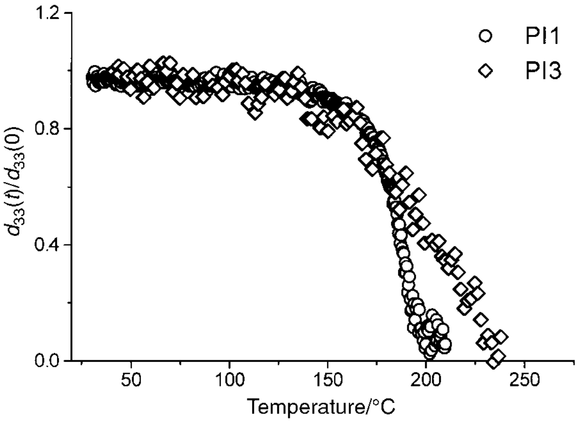


**Fig. 6** Dynamic thermal stability of NLO activity of PI1 and PI3 (temperature rate: 10 °C min$^{-1}$, in air).

maintained 90% of original nonlinearity until 150 °C. The SHG signals of both polyimides were quite stable until the temperature reached 150 °C. As the temperature reached the glass transition temperature of the polymers, fast relaxation of NLO activity was observed. PI3 showed sudden relaxation at around 170 °C corresponding to the $T_g$ of PI3. In the case of PI1, it showed a similar relaxation profile to that of PI3 despite its higher $T_g$ (198 °C). The bulkiness of the NLO chromophore should affect the thermal stability of NLO activity. The DANS chromophore of PI1 is less bulky than the hemicyanine dye containing tetraphenylborate anion of PI3. The bulkier tetraphenylborate ion prevents the aligned dipoles (hemicyanine chromophore) from reorienting to random directions.[13] So PI1 and PI3 show similar thermal stability even though PI3 has a lower $T_g$.

In conclusion, we successfully synthesized NLO-functionalized polyimides containing a hemicyanine dye. Mild Mitsunobu reaction conditions enable the incorporation of chemically labile hemicyanine dye into the polyimide backbone. These polymers showed high nonlinearity and good temporal stability. The Mitsunobu reaction is a versatile method for the synthesis of polyimides containing NLO chromophores of high $\beta$ value.

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