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# Synthesis and Characterization of Nonlinear Optical Side-Chain Polyimides Containing the Thiadiazole Chromophores

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**ABSTRACT:** Thermally stable second-order nonlinear optical (NLO) polyimides were synthesized using a standard condensation polymerization technique. The polyimides were prepared from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and pyromellitic dianhydride (PMDA) with two aromatic azo- and diazo-diamine derivatives as the NLO chromophores. The resulting polyimides were characterized by FTIR, <sup>1</sup>H-NMR, UV-vis spectroscopies, differential scanning calorimetry, thermogravimetric analysis, and gel permeation chromatography. The weight-average molecular weights of polyimides determined by gel permeation chromatography (GPC) were in the range of 32,100 to 39,300 ( $M_w/M_n = 1.58$ – $1.74$ ). All the polyimides exhibited an excellent solubility in many of the aprotic polar organic solvents, manifesting that these polyimides offer

good processability. The glass transition temperature for the resulting polyimides was in the range of 152 to 194°C and most of them showed high thermal stability. Particularly, the polyimides containing diazo group and PMDA backbone showed an enhanced thermal stability and glass transition temperature. The second harmonic generation (SHG) coefficients ( $d_{33}$ ) of the poled polyimide films range from 43.71 to 80.49 pm/V at 532 nm. Further, it is noticed that there was no SHG decay below 180°C because of the partial main-chain character of the polyimide structure, which is acceptable for nonlinear optical device applications. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1049–1058, 2012

**Key words:** NLO chromophore; polyimides; corona poling; thermal stability; SHG coefficient

## INTRODUCTION

Extensive studies have been made for the synthesis of second-order nonlinear optical (NLO) materials based on organic compounds over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, and so forth.<sup>1–5</sup> Among the organic materials, the polymeric NLO materials have been continuously drawn interest, mainly because they offer several advantages for photonic applications such as mechanical endurance, light weight, chemical resistance, and good processability for developing optical devices.<sup>6–9</sup> Theoretical and experimental studies have shown that the property of these materials should meet three main requirements: (1) large NLO responses, (2) high temporal stability of the dipole orientation, and (3) minimal optical loss (with reference to incident laser radiation). Different approaches have been developed in pursuit of these aims. In particular, very satisfactory results can be

obtained by the incorporation of suitable chromophore groups to an appropriate polymeric matrix either through dispersion or through anchoring by a covalent link.

As for the design of chromophores for second-order NLO applications, strong electron-donor and electron-acceptor substituents are commonly incorporated to a suitable conjugated bridge. The strength and the number of donor and acceptor groups as well as the nature and length of the conjugated bridge can be appropriately modulated.<sup>10–12</sup> Theoretical studies<sup>13</sup> have demonstrated that a polyene chain bridge confers better NLO properties than a polyaromatic system. However, the latter system assures high thermal stability and then is frequent in its use in the chromophores architecture. In addition, the presence of heteroatoms in the conjugated rings increases the molecular hyperpolarizability ( $\beta$ ) and a significant improvement is expected when the heterocyclic ring on the acceptor side.<sup>14</sup> The highest  $\beta$  values are obtained with the azobenzene moiety, which is followed by stilbene and benzyldiene systems.<sup>15</sup> Another approach aims to increase the  $\beta$  chromophore value by increasing the length of the bridge.<sup>12</sup>

Recently, we have synthesized several series of polyimides containing NLO chromophores by the

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easy ring opening polyaddition of dianhydrides and nitrothiazole or nitrobenzothiazole azo *m*-phenylenediamine and by the covalent binding of a chromophore onto the backbone of the polyimide via a standard condensation polymerization technique.<sup>16</sup> The resulting NLO polyimides were highly soluble in aprotic polar solvents, so the polymer solution could be spin coated on the ITO glass or other substrates to form the optical quality thin films. Secondly, these polyimides demonstrated relatively large  $d_{33}$  values range between 35.15 and 45.20 pm/V at 532 nm.

In the present study, we have made an attempt to improve the NLO properties of the recently synthesized polyimides<sup>16</sup> and their processability by increasing the conjugation length and replacing the thiazole and benzothiazole moieties with thiadiazole moiety on the acceptor side of the chromophore. Further, we report detail studies on the characterization of the resulting polyimides including the thermal and the NLO properties.

## EXPERIMENTAL

### Materials

Pyromellitic dianhydride (PMDA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from Sigma-Aldrich and were used without further purification. *N,N*-Dimethylformamide (DMF) was purified by distillation over phosphorous pentoxide. Tetrahydrofuran (THF) was purified by distillation over sodium chips and benzophenone. All the other chemicals were purchased from Loba Chemie and S. D. Fine Chem. Ltd., Mumbai, India and were used as received.

### Instruments

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet-5700 spectrometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer using tetramethylsilane (TMS) as a reference. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the polyimides were estimated by high-performance gel permeation chromatography (HP/GPC; Waters, Milford, MA). Degassed tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene (PS) standards covering the range of  $10^3$  to  $10^7$  was used for the molecular weight calibration. Ultraviolet-visible (UV-vis) spectra were measured by a Hitachi U-2800 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were respectively, performed on a Mettler-Toledo DSC 822e and Perkin-Elementer Diamond TGA/DTA thermogravimetric

analyzer at a heating rate of 10°C/min in a nitrogen atmosphere. The melting points were obtained with open capillary tubes on a Mel-Temp apparatus. Elemental analyses were performed with a Perkin Elementer PE 2400 CHN elemental analyzer. Thin polymer films were produced from 5 wt % solution of the polymer in DMF onto an indium-tin oxide (ITO) glass substrate using spin casting technique at a rate of about 1500 to 2000 rpm. Before film casting, the polymer solution was filtered through a 0.20  $\mu$ m Teflon membrane filter. All films were dried for 3 h in a vacuum oven at 100°C to remove residual solvents. The thickness and refractive indices of the polyimides were measured using a SE 850 Ellipsometer.

### Second harmonic generation (SHG) measurements

The dried film was then heated at a temperature 10°C below the glass transition temperature  $T_g$  and corona poled with an intense dc electric field as described in our earlier article.<sup>16</sup> After being poled for 1 h, the polymer film was cooled down to room temperature in the presence of the electric field. The poling conditions were as follows: high voltage, 4 KV at the needle point; gap distance  $\sim$  0.8 cm; poling current  $<0.25$  mA.

The second harmonic measurements were performed utilizing the setup as described in our earlier article.<sup>16</sup> A Mode-Locked Nd:YAG laser (Continuum Minilite-I, 6 ns pulse duration, 28 mJ maximum energy, 10 Hz repetition rate at 1064 nm) was used as a fundamental light source. The second harmonic signal generated by the *p*-polarized fundamental wavelength (1064 nm) was detected by fast photodiode (FDS010, rise time 0.9 ns, Thorlabs) and an oscilloscope (Tektronix TDS 724D, Digital Phosphor Oscilloscope) with a frequency of 500 MHz. The polymer sample was held at a 45° angle to the incident laser beam to get maximum SHG output. A standard potassium dideuterium phosphate (K\*DP) crystal was used as reference sample.

### Synthesis of chromophores

Before the synthesis of chromophores, 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole was prepared as per the procedure published elsewhere.<sup>17</sup> A mixture of *p*-nitrobenzoic acid (4.2 g, 0.025 mol), thiosemicarbazide (2.25 g, 0.025 mol), and phosphorous oxychloride (10 mL) was refluxed gently for half an hour. After cooling, water was added (25 mL) and the resulting mixture was refluxed further for 4 h and filtered. The filtrate was neutralized with 10% of KOH solution. The obtained precipitate was filtered and washed with water until the filtrate became neutral. It was then recrystallized from ethanol. The

analytical and spectral data are in good agreement with the data reported.<sup>17</sup>

### Synthesis of chromophore **a**

Three millimoles of 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole (0.66 g) was dissolved in 17 mL of glacial acetic acid. To this solution, 8 mL of sulfuric acid was added and the salt so obtained was cooled to 0°C. While stirring, sodium nitrite (0.21 g, 3 mmol) solution (10 mL) was added dropwise into the salt solution for 2 h. The mixture was stirred for another 1 h and the resulting diazonium salt solution was added slowly into *m*-phenylenediamine (0.32 g, 3 mmol), which was dissolved in 1 mL of hydrochloric acid and 10 mL of water. The reaction temperature was maintained below 0°C. After stirring for another 1 h, the solution was neutralized with 50% ammonia. The resulting precipitate was filtered and washed several times with water till the filtrate was neutral. It was finally subjected to column chromatography over SiO<sub>2</sub> with benzene and ethylacetate (1 : 1) as an eluate and obtained 0.76 g yield (75%) of **a**.

m.p.: 209–210°C.  $\lambda_{\text{max}}$  (DMF): 363 nm. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 3.61 (s, 4H, ArNH<sub>2</sub>), 6.94 (s, 1H, ArH), 7.11 (s, 1H, ArH), 7.28 (s, 1H, ArH), 7.99 (d, *J* = 6.8 Hz, 2H, ArH), 8.29 (d, *J* = 7.1 Hz, 2H, ArH). FTIR (KBr, cm<sup>-1</sup>): 3426, 3279 (w, N-H), 1591 (s, N = N), 1509, 1340 (versus, N = O). ANAL. Calcd for C<sub>14</sub>H<sub>11</sub>N<sub>7</sub>O<sub>2</sub>S: C, 49.27%; H, 3.22%; N, 28.74%. Found: C, 49.15%; H, 3.29%; N, 28.81%.

### Synthesis of chromophore **b**

To a 15 mL of 1N HCl solution containing freshly prepared aniline (7 mmol) was added an equal molar amount of 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole diazonium salt in an ice bath with vigorous stirring for 1 h followed by stirring at 50°C under N<sub>2</sub> atmosphere for 1 h; then, the mixture was neutralized with 50% ammonia. After stirring for another 1 h, the resulting precipitate was filtered and washed several times with water until the filtrate was neutral and dried. The crude product was recrystallized from ethanol/DMF (4 : 1) and the purified product 4-[2-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)diazenyl]phenylamine was obtained.

This compound was used for the synthesis of chromophore **b** as per the procedure adopted for **a**.

Yield: 63%. m.p.: 178–179°C.  $\lambda_{\text{max}}$  (DMF): 374 nm. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 3.56 (s, 4H, ArNH<sub>2</sub>), 5.83 (s, 1H, ArH), 6.15 (s, 1H, ArH), 6.50 (s, 1H, ArH), 7.40 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.86 (s, 1H, ArH), 8.00 (s, 1H, ArH), 8.36 (s, 1H, ArH). FTIR (KBr, cm<sup>-1</sup>): 3350, 3209 (w, N-H), 1598 (s, N = N), 1506, 1359 (versus, N = O). ANAL. Calcd for

C<sub>20</sub>H<sub>15</sub>N<sub>9</sub>O<sub>2</sub>S: C, 53.92%; H, 3.39%; N, 28.30%. Found: C, 54.01%; H, 3.31%; N, 28.24%.

The chemical reaction routes of chromophores **a** and **b** are shown in Figure 1.

### Synthesis of polyimides

#### Synthesis of polyimide **Ia**

Chromophore **a** (0.34 g, 1 mmol) was dissolved in 5 mL of anhydrous DMF at room temperature and was followed by the addition of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (0.44 g, 1 mmol) at once. The resulting solution was stirred at room temperature for 12 h. To this solution, a mixture of acetic anhydride and pyridine (8 mL/4 mL, 2 : 1) was added and the stirring was continued for 12 h at room temperature. While stirring, it was then heated to 90°C under nitrogen atmosphere for 3 h. The polymer thus obtained was precipitated into methanol and collected by filtration. It was further purified by dissolution in THF and was reprecipitated into methanol. The resulting polyimide **Ia** was collected and washed with methanol in a Soxhlet extractor for 24 h and dried in *vacuo* at 60°C for 48 h.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 6.75 (d, 1H, ArH), 7.36 (s, 1H, ArH), 7.73 (d, 1H, ArH), 7.85 (d, 1H, ArH), 7.95 (s, 1H, ArH), 8.27 (d, 1H, ArH), 8.36 (q, 4H, ArH). FTIR (KBr, cm<sup>-1</sup>): 1788, 1735 (s, C=O), 1600 (s, N = N), 1525, 1345 (versus, N = O), 1371 (m, C–N), 721 (s, imide ring). ANAL. Calcd for (C<sub>33</sub>F<sub>6</sub>H<sub>13</sub>N<sub>7</sub>O<sub>6</sub>S)<sub>*n*</sub>: C, 52.88%; H, 1.75%; N, 13.08%. Found: C, 52.97%; H, 1.71%; N, 13.01%.

A similar procedure was adopted for the synthesis of polyimides **Ib**, **Ia** and **Ib**.

#### Synthesis of polyimide **Ib**

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.81 (d, 1H, ArH), 7.90 (s, 1H, ArH), 8.00 (d, 1H, ArH), 8.06 (d, 1H, ArH), 8.13 (s, 1H, ArH), 8.32 (m, 7H, ArH), 8.60 (d, 2H, ArH). FTIR (KBr, cm<sup>-1</sup>): 1782, 1726 (s, C=O), 1598 (s, N = N), 1525, 1340 (versus, N = O), 1371 (m, C–N), 722 (s, imide ring). ANAL. Calcd for (C<sub>39</sub>F<sub>6</sub>H<sub>17</sub>N<sub>9</sub>O<sub>6</sub>S)<sub>*n*</sub>: C, 54.87%; H, 2.01%; N, 14.76%. Found: C, 54.78%; H, 2.07%; N, 14.81%.

#### Synthesis of polyimide **Ia**

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.85 (s, 1H, ArH), 8.00 (m, 2H, ArH), 8.24 (m, 5H, ArH). FTIR (KBr, cm<sup>-1</sup>): 1789, 1732 (s, C=O), 1598 (s, N = N), 1521, 1342 (versus, N = O), 1382 (m, C–N), 719 (s, imide ring). ANAL. Calcd for (C<sub>24</sub>H<sub>9</sub>N<sub>7</sub>O<sub>6</sub>S)<sub>*n*</sub>: C, 55.07%; H, 1.74%; N, 18.73%. Found: C, 55.17%; H, 1.68%; N, 18.67%.

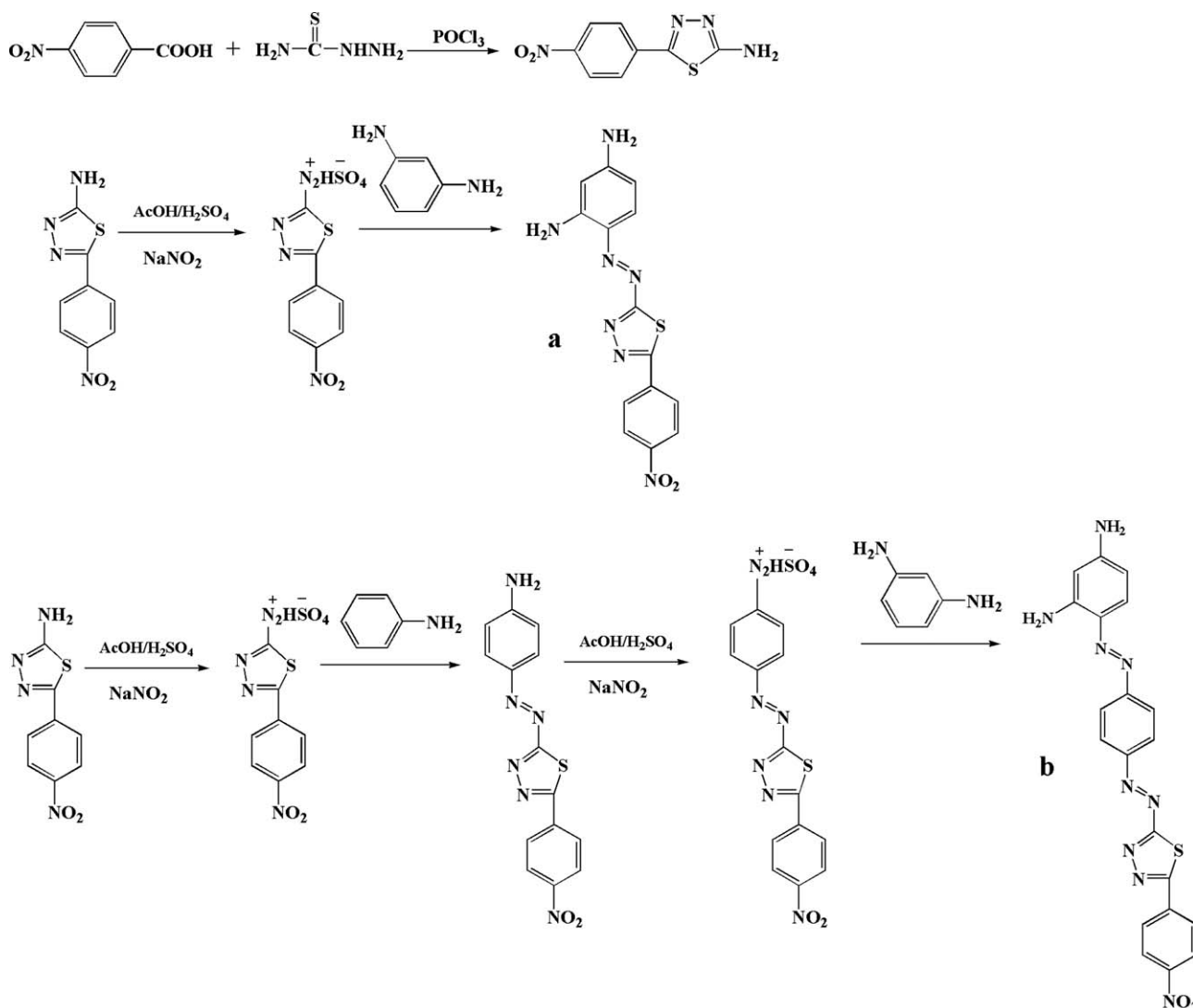


Figure 1 Synthetic route for chromophores.

### Synthesis of polyimide **Ib**

$^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ ,  $\delta$ ): 6.73 (d, 1H, ArH), 7.16 (d, 1H, ArH), 7.40 (s, 1H, ArH), 7.95 (s, 1H, ArH), 8.24 (m, 4H, ArH), 9.33 (m, 4H, ArH). FTIR (KBr,  $\text{cm}^{-1}$ ): 1777, 1729 (s, C=O), 1598 (s, N=N), 1523, 1346 (versus, N=O), 1372 (m, C-N), 722 (s, imide ring). ANAL. Calcd for  $(\text{C}_{30}\text{H}_{13}\text{N}_9\text{O}_6\text{S})_n$ : C, 57.42%; H, 2.08%; N, 20.09%. Found: C, 57.31%; H, 2.14%; N, 20.15%.

The chemical reaction routes of polyimides **Ia**, **Ib**, **IIa**, and **IIb** are presented in Figure 2.

## RESULTS AND DISCUSSION

### Synthesis and characterization of chromophores

The new chromophores **a** and **b** were synthesized starting from 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole as shown in Figure 1. The chemical structures of the synthesized chromophores were confirmed by

FTIR,  $^1\text{H-NMR}$ , UV-vis, and elemental analyses. FTIR spectra clearly show the characteristic absorption peaks of amino group at around 3400 and 3200  $\text{cm}^{-1}$ , while the azo group at around 1590  $\text{cm}^{-1}$ . The characteristic asymmetric and symmetric absorption peaks of nitro group appeared at around 1510 and 1340  $\text{cm}^{-1}$ , respectively. The DMF solutions of chromophores **a** and **b** showed strong UV absorption bands with maxima at 363 and 374 nm, respectively.

The analytical and spectral data confirmed the expected chemical structures. These chromophores are soluble in many common organic solvents such as acetone, THF, cyclohexanone, DMF, *N,N*-dimethylacetamide (DMAc), dimethylsulphoxide (DMSO) and *N*-methyl-2-pyrrolidinone (NMP). These NLO chromophores are push-pull type compounds with an amino group as the electron-donor and the nitro group as the electron-acceptor linked through azo conjugated bridge (see Fig. 1).



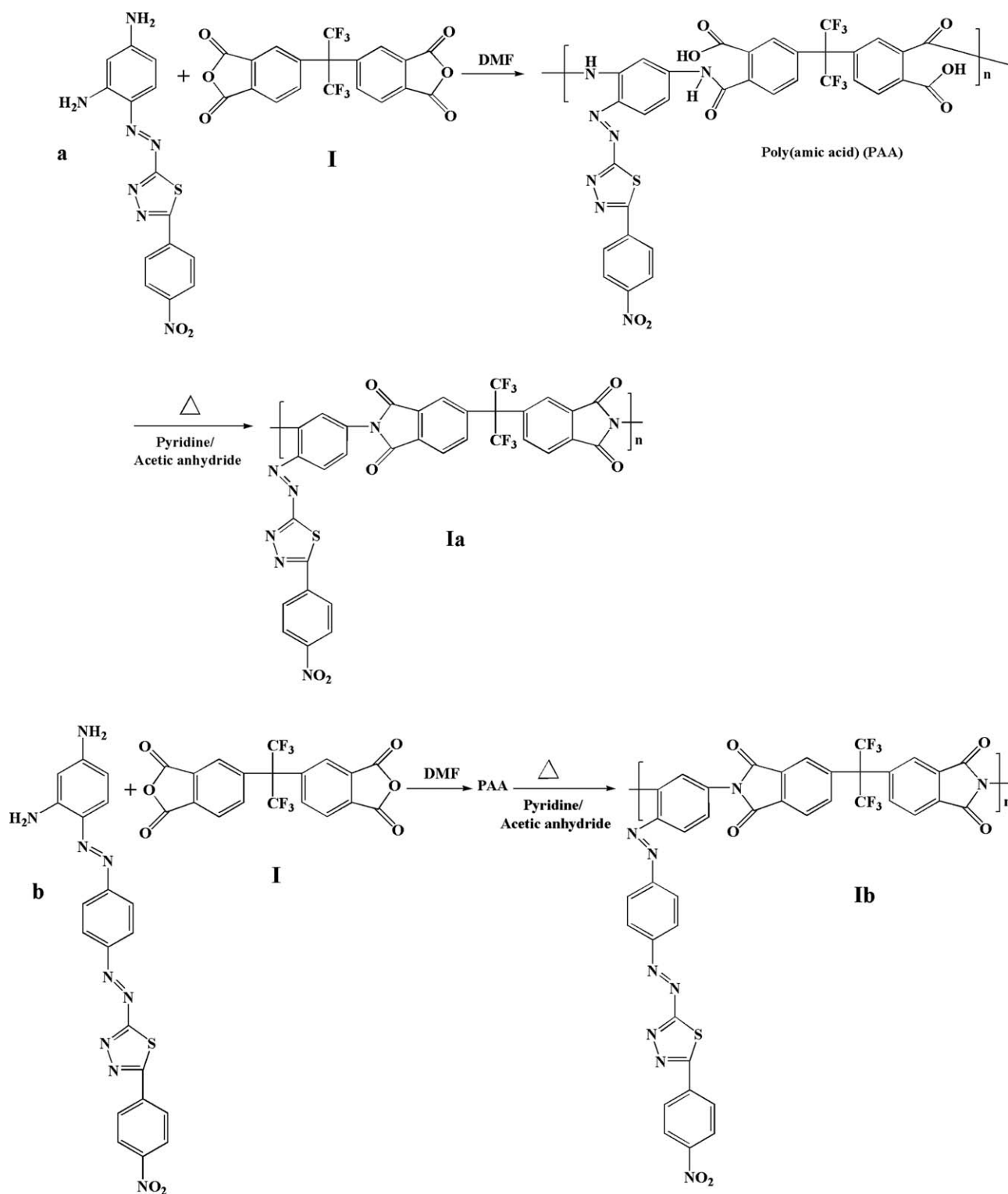


Figure 2 Synthetic route for polyimides.

### Synthesis and characterization of polyimides

Polyimides were prepared by a two-step process as shown in Figure 2. A diamino chromophore reacts with dianhydride monomer in DMF at room temperature to yield poly(amic acid), followed by treating

with pyridine and acetic anhydride at ambient temperature. The resulting polyimides were purified by Soxhlet extraction with methanol to remove low-molecular weight portions. The structures of these polyimides were characterized using FTIR,  $^1\text{H-NMR}$ ,

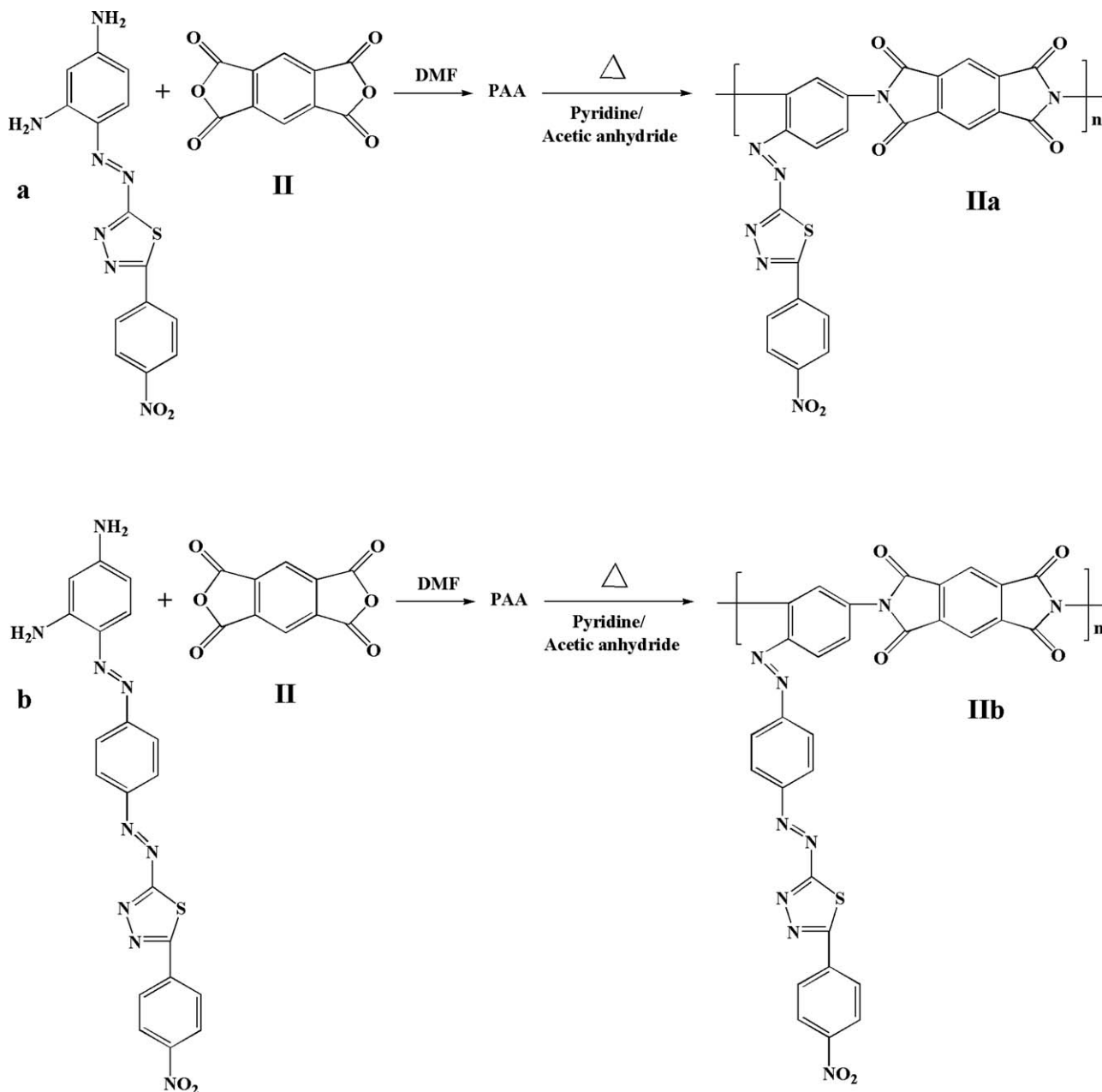


Figure 2 (Continued from the previous page)

GPC, and elemental analyses. The FTIR spectra as shown in Figure 3 show the characteristic absorption bands at around 1780 and 1730  $\text{cm}^{-1}$  are respectively, assigned to asymmetric and symmetric C=O stretchings. The C—N stretching in the imide groups appeared at around 1370  $\text{cm}^{-1}$  and a band appeared at around 720  $\text{cm}^{-1}$  are attributed to imide ring. The characteristic asymmetric and symmetric stretchings appeared at around 1520 and 1340  $\text{cm}^{-1}$  are respectively, assigned to nitro groups. The chemical shifts in the  $^1\text{H}$ -NMR spectra of polyimides **Ia**, **IIa**, **Ib**, and **IIb** were assigned based on the comparison with those of the corresponding NLO chromophores

**a** and **b**. For Polyimides **Ia** and **IIa**, the chemical shifts for aromatic protons appeared at 6.75, 7.35, 7.75, 8.00, and 8.25 ppm. Similarly, the chemical shifts for **Ib** and **IIb** were appeared at 6.70, 7.15, 7.40, 7.80, 7.95, 8.15, and 8.60 ppm. All these data indicated the imidization of poly(amic acid) and the presence of NLO moiety in the polyimides.

The molecular weights of the polyimides were determined by GPC with polystyrene as the standard and THF as the eluent, and the data so obtained were presented in Table I. The polydispersities were in the range of 1.58–1.74. The elemental analyses data fit the structures of polyimides. All these results

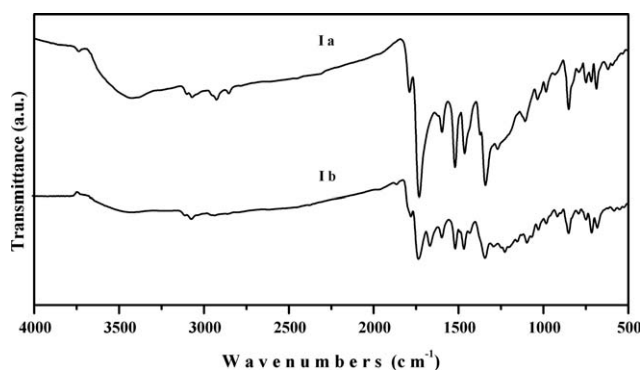


Figure 3 FTIR spectra of polyimides **Ia** and **Ib**.

were consistent with the proposed structures, indicating that the NLO chromophores remained intact during the polymerization. These polyimides are highly soluble in aprotic polar solvents such as cyclohexanone, DMF, DMAc, DMSO, and NMP. Further, polyimides **Ia** and **Ib** synthesized from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride are even soluble in THF and acetone. This is due to the presence of flexible- $\text{CF}_3$  groups in the polyimide backbone. The incorporation of fluorinated groups into a polyimide backbone enhanced its solubility. Owing to their solubility, these polyimides offer good processability and hence, optical quality thin films can be easily prepared from their solutions.<sup>18,19</sup>

### Thermal and nonlinear optical properties

The thermal behavior of the polyimides was examined with DSC and TGA measurements. From Figure 4, it is observed that no thermal transitions were noticed between 60 and 150°C. Polyimides containing diazo chromophores exhibited higher  $T_g$  values than the corresponding azo containing chromophores. All the PMDA polyimides revealed a higher  $T_g$  in comparison with that of the corresponding 6FDA ones, because of a higher rigidity of the polymer backbone. The polyimide **Iib** exhibited a high  $T_g$  ( $\sim 194^\circ\text{C}$ ), reflecting the stable NLO diazo *m*-phenylenediamine structure.

The differential branching structure analysis (TGA) on the obtained polyimides was carried out and resulting thermograms are presented in Figure 5. The diazo polyimides **Ib** and **Iib** have obviously showed better thermal stability than the azo polyimides **Ia** and **Iia**, respectively. It was, therefore, expected that the thermal stability of the NLO chromophore, would improve the stability of the final NLO polyimide. The polyimides **Ia** and **Ib**, however, were less thermally stable than the corresponding polyimides with the same chromophores. This is because of the flexible groups ( $-\text{CF}_3$ ) in the polyimide backbone.

Noncentrosymmetry in the polyimide films was induced by a corona poling at a temperature  $10^\circ\text{C}$  below the glass transition temperature. After the electric poling, the dipole moments of the NLO chromophores were aligned along the direction of the electric field and thereby, the maximum absorbances were reduced due to birefringence. The UV-vis absorption spectra of the polyimide **Ia** before and after poling are presented in Figure 6. The poling efficiency was determined using the order parameter ( $\Phi = 1 - A_1/A_0$ , where  $A_0$  and  $A_1$  are the absorbances of the polymer film before and after poling, respectively). The order parameter of polyimide **Ia** was found to be 0.21 and the estimated order parameters for the remaining polyimides are presented in Table I. All these data suggested that polyimides were efficiently poled and as a result, the chromophores were effectively aligned since the order parameter describes the chromophore alignment and correlates to the NLO properties of the polyimides.

The basic requirement for the second-order nonlinear optical process is that the material must be noncentrosymmetric. This can be easily achieved by corona poling at a temperature close to glass transition temperature, so that the molecular dipoles in the polymer can be oriented. After the polymer film is poled, it becomes second-order NLO active. The most convenient technique to study the second-order NLO activity is to study the second harmonic generation (SHG) processes, characterized by  $d_{33}$ , an SHG coefficient.

TABLE I  
Physical and NLO Properties of Polyimides

Polyimides	$M_n^a$	$M_w^a$	$\lambda_{\text{max}}^b$ (nm)	$T_g$ ( $^\circ\text{C}$ )	$T_d^c$ ( $^\circ\text{C}$ )	$\Phi^d$	Film thickness ( $\mu\text{m}$ )	$d_{33}$ (pm/V)
<b>Ia</b>	20,200	32,100	360	152	284	0.21	0.07	80.49
<b>Ib</b>	21,100	35,500	362	181	345	0.10	0.07	43.71
<b>Iia</b>	21,800	37,200	360	160	324	0.16	0.10	44.91
<b>Iib</b>	22,500	39,300	345	194	351	0.11	0.09	75.24

<sup>a</sup> Measured by GPC in THF using polystyrene as a standard.

<sup>b</sup> Polymer film after corona poling.

<sup>c</sup> Decomposition temperature measured with TGA at 15 wt % under nitrogen atmosphere at a scan rate of  $10^\circ\text{C}/\text{min}$ .

<sup>d</sup> Order parameter.



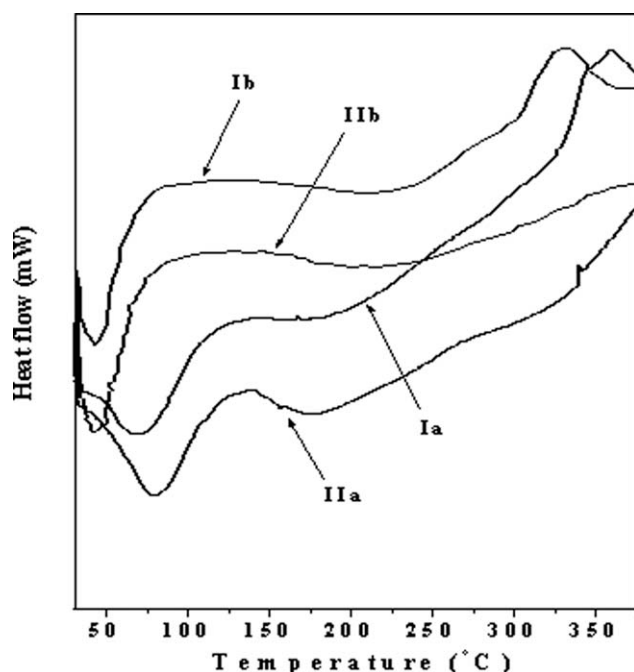


Figure 4 DSC thermograms of polyimides at a heating rate of 10°C/min under a nitrogen atmosphere.

The second-order NLO coefficient ( $d_{33}$ ) for the poled polyimide was calculated based on the following equation.<sup>20</sup>

$$\frac{d_{33,s}}{d_{36,k}} = \frac{\chi_s^{(2)}}{\chi_k^{(2)}} = \sqrt{\frac{I_s}{I_k}} \frac{l_{c,k}}{l_s} F$$

where  $d_{36,k}$  is the  $d_{36}$  of K\*DP crystal, which is 0.40 pm/V;  $I_s$  and  $I_k$  are the SHG intensities of polyimide sample and K\*DP crystal, respectively;  $l_{c,k}$  is the coherence length of the K\*DP crystal (11.4  $\mu\text{m}$ );  $l_s$  is

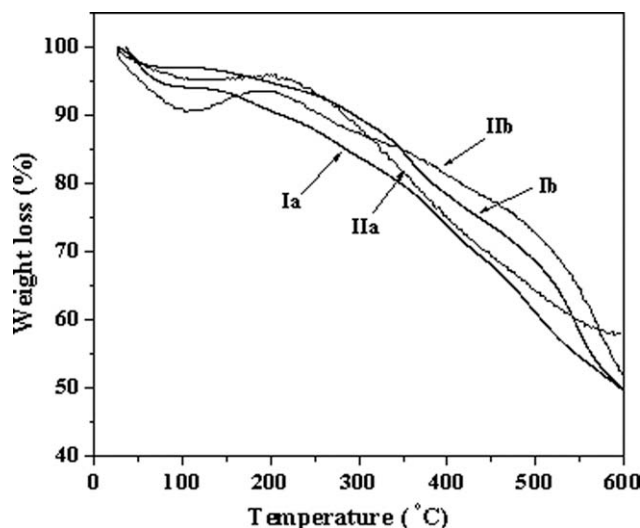


Figure 5 TGA thermograms of polyimides at a heating rate of 10°C/min under a nitrogen atmosphere.

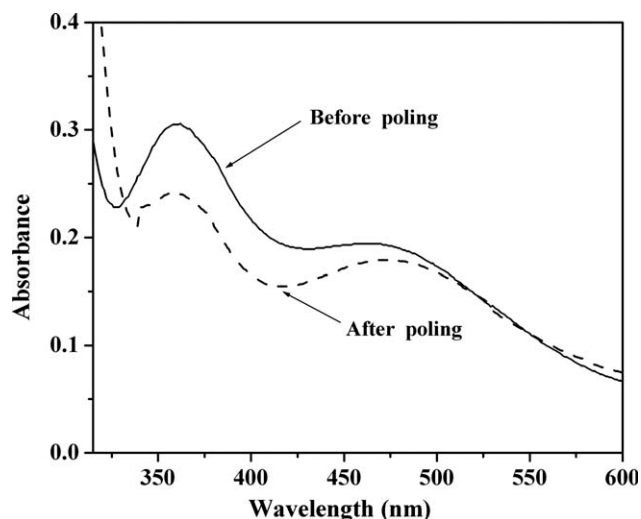
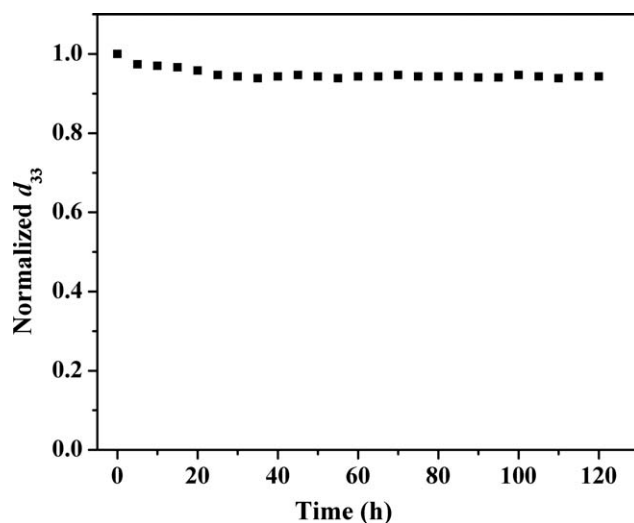


Figure 6 UV-vis absorption spectra of polyimide Ia before and after poling.

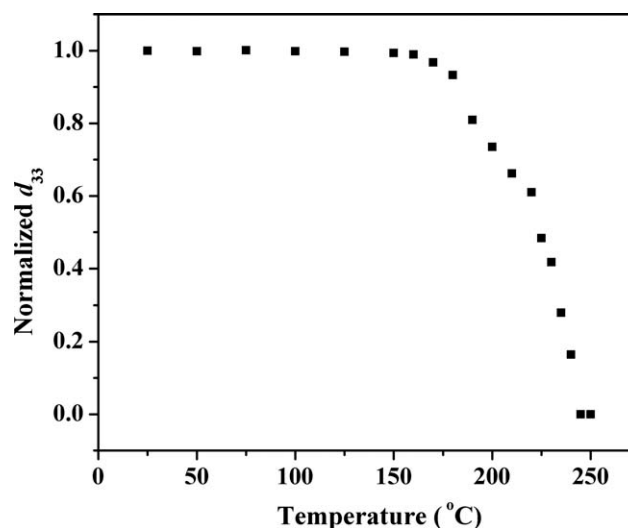
the thickness of the polyimide sample; and  $F$  is the correction factor, which is approximately equal to 1.2 when  $l_{c,k} \gg l_s$ . The calculated  $d_{33}$  values of these polyimides at the wavelength of 532 nm are included in Table I. It is observed that all the polyimides exhibited  $d_{33}$  values in the range of 43.71 to 80.49 pm/V signifying that polyimides showed enhanced resonance with reference to a 1.0 mm thick K\*DP crystal. The resulting  $d_{33}$  values are much superior to those of the dialkylaminonitrostilbene (DANS)-substituted NLO polymer system.<sup>21</sup>

The thermal relaxation process of the dipole orientation is directly related to the  $T_g$  of the polymer. A high  $T_g$  implies a higher orientational stability. To probe this stability, we monitored the temporal and thermal stability of the second harmonic generations for all the polyimides. At room temperature, all of the polyimides are stable and there was no decay in the intensity of the SHG signal. At 100°C in air, after an initial decay to  $\sim 94\%$  of the original signal, more than 90% of the SHG signal was remained stable till 120 h for polyimide Ia as can be seen in Figure 7. Figure 8 demonstrates the SHG signals of polyimides Ib and IIb measured at 150°C in air for 130 h. It is clearly revealed that SHG signals of Ib and IIb are stable for 130 h even at higher temperature. However, the initial signals of Ib and IIb decayed only by  $\sim 25$  and 15%, respectively.

To evaluate the high-temperature stability of the polyimides, we have studied the temporal stability of the SHG signal for all the polyimides. Figure 9 represents the dynamic thermal stability of the NLO activity of the polyimide IIb. To investigate the real time NLO decay of the SHG signal of the poled polyimide films as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 5°C/min from 25 to 250°C. The poled film of



**Figure 7** Temporal stability of the SHG signal of polyimide **Ia** at 100°C in air.



**Figure 9** The SHG signal of polyimide **IIb** as a function of temperature.

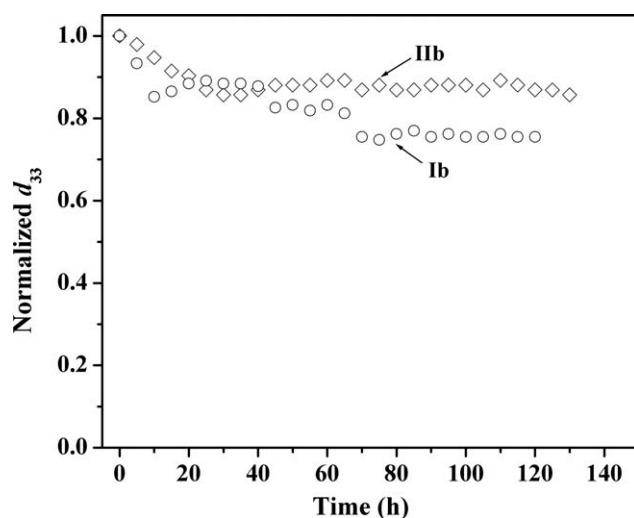
polyimide **IIb** exhibited a greater thermal stability and the SHG signal was stable up to 180°C, as can be clearly seen from Figure 9. A fast decay of the SHG signal was observed when the temperature was close to the polyimide's  $T_g$  (194°C). The signal was completely disappeared as the temperature went above the  $T_g$ . However, it was found that the same magnitude of the SHG signal can be recovered from this sample after it was reoled by corona discharging, indicating that the NLO chromophore was not damaged after experiencing high temperatures. Similar results were observed with polyimides **Ia**, **IIa**, and **Ib**. The obtained thermal characteristics and their optical nonlinearities clearly indicate that these polyimides may be useful for practical applications. Especially **Ib** and **IIb** may be the most promising

candidates based on their processability, stability and NLO activity.

## CONCLUSIONS

Azo and diazo containing nitro substituted thiadiazoles were newly synthesized and characterized. With these two chromophores, a series of second-order NLO functionalized polyimides were prepared from 6FDA and PMDA using a standard condensation polymerization technique. Analytical and spectral data were found to be consistent with the proposed structures of polyimides. All the polyimides exhibited an excellent solubility in many of the aprotic polar solvents, manifesting that these polyimides offer good processability and hence, optical quality thin films can be easily prepared from their solutions. Among the polyimides synthesized, polyimides containing 6FDA demonstrated an excellent solubility owing to the presence of flexible  $-\text{CF}_3$  groups in the polyimide backbone. Both diazo group and PMDA backbone enhanced the thermal stability and  $T_g$  of the polyimides. The developed polyimides relatively exhibited large  $d_{33}$  values range from 43.71 to 80.49 pm/V at 532 nm. Further, it was noticed that as the stability of the NLO chromophore increased, the glass transition temperatures (up to 194°C) of the polyimides increased accordingly. Thermal characteristic and optical nonlinearities clearly demonstrated that these polyimides are useful for practical applications.

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**Figure 8** Temporal stability of the SHG signals of polyimides **Ib** and **IIb** at 150°C in air.

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