

Novel Aromatic Polyimides for Nonlinear Optics

Dong Yu, Ali Gharavi, and Luping Yu*

Contribution from the Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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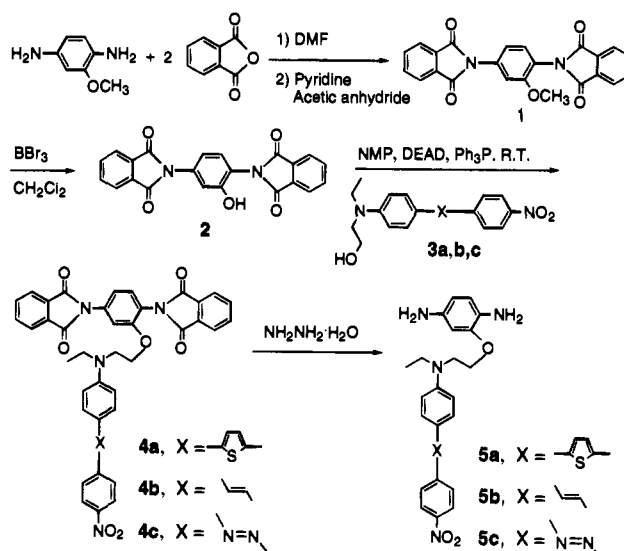
Abstract: A general approach to the synthesis of second-order nonlinear optical (NLO) polyimides exhibiting high thermal stability has been developed. Several selected NLO chromophores have been incorporated into the polyimide backbone. Detailed physical studies showed that these polymers are very promising for practical applications. Three of these polyimides are soluble in common organic solvents, offering the ease of processing. High glass temperatures, around 230 °C, assure a long-term NLO stability at elevated temperatures, such as 150 °C. Low optical loss was observed for those soluble polymers. The synthetic approach is also versatile and will allow the syntheses of many other functional polymers.

Introduction

Second-order nonlinear optical (NLO) polymers have been studied for more than a decade.^{1–3} It is known that there are three important issues preventing these materials from practical applications: that is, the instability of the dipole orientation, inadequate optical nonlinearity, and high optical loss.^{2,3} Although it is extremely difficult to synthesize materials which will solve all of these problems, they are being ameliorated by a tremendous research effort by different research groups.^{2,3} Numerous approaches have been developed to tackle these issues and the performances of polymers thus developed have been greatly enhanced. For example, various cross-linkable or high glass transition temperature polymers were developed to enhance the stability of dipole orientation at elevated temperatures.^{2–10} New chromophores with improved optical nonlinearity and thermal stability have been developed.¹¹ The origin of optical loss in some of the NLO polymers has been studied which will help to design strategies to minimize it.¹² Polymers exhibiting high thermal stability and large second-order optical nonlinearity are appearing in literature and are of great interest in applications of opto-electronic devices.^{2,3}

Among these polymer systems, polyimides, especially functionalized aromatic polyimides, have shown promising potential for the purpose of device applications.^{4–8} Recently, we have developed a generic approach to synthesize novel functionalized polyimides for second-order NLO properties. This paper reports the detailed syntheses and characterizations of different polyimides. It was found that these polyimides exhibit a high glass

Scheme 1. Synthesis of Diamino Monomers



transition temperature ($T_g \sim 230$ °C), a long-term stability at elevated temperatures (e.g., at 150 °C), and low optical loss (2 dB/cm at 632 nm). The thermal characteristics of these polyimides meet the requirements for device applications as outlined by engineers. An attempt has been made to establish the structure/property relationship among a series of these related polymers.

Experimental Section

All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated except for tetrahydrofuran (THF) which was distilled over sodium benzophenone ketyl. The numbering of the compounds is shown in Schemes 1–3.

Compound 1. To a stirred solution of 2,5-diaminoanisole (22.6 g, 163.8 mmol) in 50 mL of anhydrous DMF was added the phthalic anhydride (60 g, 405.1 mmol) at room temperature under nitrogen. The mixture was stirred at 25 °C for 1 h, followed by the addition of 70 mL of acetic anhydride, 35 mL of pyridine, and 20 mL of DMF. After being stirred for 1 h, the mixture was heated at 90 °C for 4 h. White solids precipitated out from the reaction medium after the reaction mixture was cooled down. The product was collected by filtration and recrystallized from DMF (60.0 g, 92%, mp 273–274 °C). ¹H NMR (DMSO-*d*₆, ppm): δ 3.73 (s, -OCH₃, 3 H), 7.16 (d, *J* = 8.2 Hz, ArH, 1 H), 7.34 (s, ArH, 1 H), 7.50 (d, *J* = 8.3 Hz, ArH, 1 H), 7.90 (m, ArH, 4 H), 7.96 (m, ArH, 4 H).

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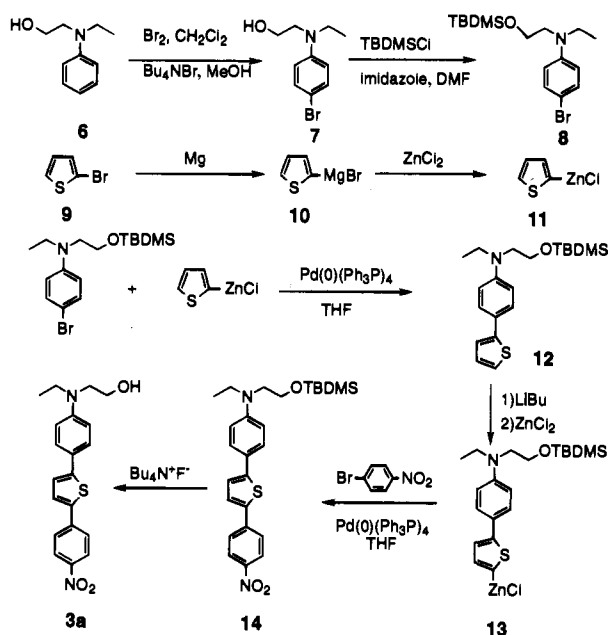
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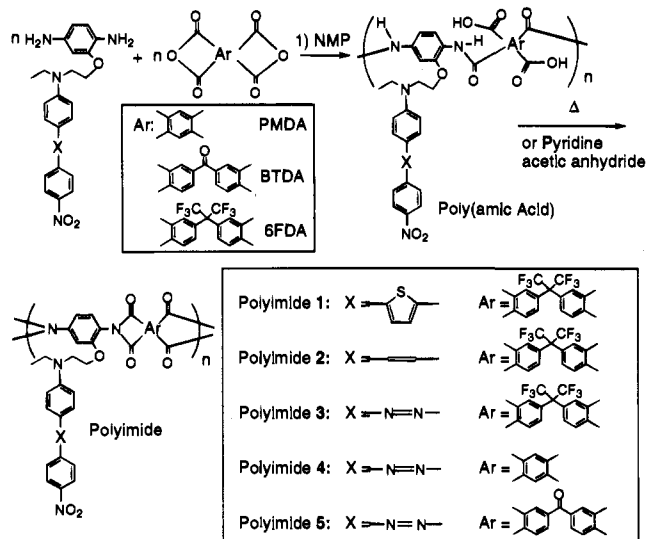
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Scheme 2. Synthesis of Compound 3a



Scheme 3. Synthesis of Poly(amic acid)s and Polyimides



Compound 2. Boron tribromide (19.9 mL, 52.8 g, 210.9 mmol) was added dropwise at -78°C to a mixture of compound 1 (12.0 g, 30.1 mmol) in 100 mL of distilled dichloromethane. After the mixture was stirred for 1 h at -78°C and 12 h at room temperature, the reaction mixture was hydrolyzed by adding water dropwise. The white solid was collected, washed with water, and then recrystallized from DMF (11.5 g, 99%, mp $323\text{--}324^\circ\text{C}$). $^1\text{H NMR}$ (DMSO- d_6): δ 6.97 (d, $J = 7.9$ Hz, ArH, 1 H), 7.06 (s, ArH, 1 H), 7.37 (d, $J = 7.9$ Hz, ArH, 1 H), 7.88 (m, ArH, 4 H), 7.94 (m, ArH, 4 H), 10.21 (s, ArOH, 1 H).

Compound 7. Methanol (0.5 equiv, 4.85 g, 152 mmol), 0.01 equiv of tetrabutylammonium bromide (0.98 g, 3 mmol), and bromine (15.6 mL, 48.43 g, 303 mmol) were added to a stirred solution of *N*-ethyl-*N*-(β -hydroxyethyl)aniline (50 g, 303 mmol) in 100 mL of dichloromethane. The solution was stirred overnight and then poured into a saturated sodium acetate solution. The mixture was extracted twice by dichloromethane (40 mL each time). The organic layer was dried over anhydrous sodium sulfate. After the removal of the solvent, the mixture was separated using a silica chromatography column (silica gel, hexane-ethyl acetate (1/1)) to give compound 7 (65 g, 88%). $^1\text{H NMR}$ (CDCl₃): δ 1.12 (t, $J = 7.1$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 3.34 (q, $J = 7.1$ Hz, $-\text{CH}_2\text{CH}_3$, 2 H), 3.38 (t, $J = 6.0$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$, 2 H), 3.72 (t, $J = 6.0$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$, 2 H), 6.57 (d, $J = 8.7$ Hz, ArH, 2 H), 7.22 (d, $J = 8.7$ Hz, ArH, 2 H).

Compound 8. Compound 7 (34.35 g, 141 mmol) in 20 mL of *N,N*-dimethylformamide was added dropwise to a 500-mL two-necked round-bottomed flask containing *tert*-butyldimethylsilyl chloride (25.45 g, 169 mmol), imidazole (23.95 g, 352 mmol), and 40 mL of *N,N*-dimethylformamide under nitrogen. After 12 h, the mixture was poured into water and extracted twice by 30 mL of ether. The organic layer was dried over sodium sulfate. After the removal of the solvent, the mixture was chromatographed (hexane-ethyl acetate (10:1)) to give 8 (45.4 g, 90%). $^1\text{H NMR}$ (CDCl₃): δ 0.05 (s, $-\text{Si}(\text{CH}_3)_2$, 6 H), 0.85 (s, $-\text{Si}(\text{CH}_3)_3$, 9 H), 1.09 (t, $J = 7.2$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 3.33 (m, 4 H), 3.67 (t, $J = 6.3$ Hz, $-\text{CH}_2\text{CH}_2\text{O}-$, 2 H), 6.47 (d, $J = 8.8$ Hz, ArH, 2 H), 7.16 (d, $J = 8.8$ Hz, ArH, 2 H).

Compound 12. 2-Bromothiophene (13.65 g, 83.7 mmol) and magnesium powder (2.24 g, 92 mmol) were added to 30 mL of THF in a 250-mL flask under nitrogen. The mixture was stirred at room temperature for 2 h and then anhydrous zinc chloride (12.55 g, 92 mmol) was added at 0°C . The mixture was stirred for another 1 h and compound 8 (20 g, 55.8 mmol) in 20 mL of THF was added dropwise to the resulting organozinc reagent 11. A catalytic amount of Pd(0)(Ph₃P)₄ (1.67 g, 1.4 mmol) was then added and the resulting reaction mixture was refluxed overnight. After removing the solid by filtration, the reaction mixture was concentrated and separated by a flash column (hexane as eluent) to give 12 (12.6 g, 63%). $^1\text{H NMR}$ (CDCl₃, ppm): δ 0.05 (s, $-\text{Si}(\text{CH}_3)_2$, 6 H), 0.89 (s, $-\text{Si}(\text{CH}_3)_3$, 9 H), 1.16 (t, $J = 7.0$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 3.41 (m, 4 H), 3.74 (t, $J = 6.4$ Hz, $-\text{CH}_2\text{CH}_2\text{O}-$, 2 H), 6.62 (d, $J = 8.7$ Hz, ArH, 2 H), 6.96 (t, $J = 4.2$ Hz, thienyl proton, 1 H), 7.06 (d, $J = 4.2$ Hz, thienyl protons, 2 H), 7.39 (d, $J = 8.7$ Hz, ArH, 2 H).

Compound 14. Butyl lithium (16.4 mL, 1.6 M in hexane, 26.3 mmol) was added through a syringe needle at -78°C to a solution of compound 12 (9.5 g, 26.3 mmol) in 100 mL of THF. After the addition, the reaction flask was warmed up to room temperature for 2 h. The reaction mixture was transferred to the solution of the anhydrous zinc chloride (3.94 g, 28.9 mmol) in 50 mL of THF. 1-Bromo-4-nitrobenzene (5.31 g, 26.3 mmol) and Pd(0)(Ph₃P)₄ (1.0 g, 0.9 mmol) was added to the resulting green solution. The mixture was stirred overnight and poured into water. The resulting red solid was collected by filtration and recrystallized from chloroform/MeOH to give compound 14 (8.0 g, 63%, mp $131\text{--}134^\circ\text{C}$). $^1\text{H NMR}$ (CDCl₃, ppm): δ 0.05 (s, $-\text{Si}(\text{CH}_3)_2$, 6 H), 0.90 (s, $-\text{Si}(\text{CH}_3)_3$, 9 H), 1.18 (t, $J = 7.1$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 3.44 (m, 4 H), 3.76 (t, $J = 6.2$ Hz, $-\text{CH}_2\text{CH}_2\text{O}-$, 2 H), 6.65 (d, $J = 8.6$ Hz, ArH, 2 H), 7.11 (d, $J = 3.4$ Hz, thienyl proton, 1 H), 7.37 (d, $J = 3.5$ Hz, thienyl proton, 1 H), 7.43 (d, $J = 8.6$ Hz, ArH, 2 H), 7.65 (d, $J = 8.6$ Hz, ArH, 2 H), 8.16 (d, $J = 8.6$ Hz, ArH, 2 H). Anal. Calcd for C₂₆H₃₄N₂O₃SSi: C, 64.69; H, 7.10; N, 5.80; S, 6.64. Found: C, 64.75; H, 7.12; N, 5.81; S, 6.74.

Compound 3a. The tetrabutylammonium fluoride (21 mL, 1.0 M solution in THF, 21 mmol) was added dropwise to the solution of compound 14 in 50 mL of THF. After being stirred for 4 h, the solution was poured into water; the red solid was collected by filtration and recrystallized from chloroform/MeOH to give 3a (5.1 g, 98%, mp $190\text{--}193^\circ\text{C}$). $^1\text{H NMR}$ (CDCl₃, ppm): δ 1.19 (t, $J = 7.0$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 1.64 (t, $J = 5.7$ Hz, $-\text{OH}$, 1 H), 3.45 (q, $J = 7.0$ Hz, $-\text{CH}_2\text{CH}_3$, 2 H), 3.50 (t, $J = 5.7$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$, 2 H), 3.81 (t, $J = 5.7$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$, 2 H), 6.73 (d, $J = 8.8$ Hz, ArH, 2 H), 7.12 (d, $J = 8.7$ Hz, ArH, 2 H), 7.65 (d, $J = 8.7$ Hz, ArH, 2 H), 8.15 (d, $J = 8.6$ Hz, ArH, 2 H). Anal. Calcd for C₂₀H₂₀N₂O₃S: C, 65.20; H, 5.47; N, 7.60; S, 8.70. Found: C, 65.26; H, 5.47; N, 7.52; S, 8.76.

Compound 4. A general procedure for the syntheses of compounds 4a, 4b, and 4c is as follows. Compound 4 (2.9 mmol) was completely dissolved in 15 mL of anhydrous NMP under nitrogen. After the addition of 1 equiv of compound 3 and 5.7 mmol of triphenylphosphine, diethyl azodicarboxylate (0.9 mL, 5.7 mmol) in 5 mL of anhydrous NMP was added dropwise. The reaction mixture was stirred at room temperature for 8 h, and then precipitated into 100 mL of methanol. The resulting precipitate was collected by filtration and recrystallized from chloroform/MeOH.

Compound 4a: 87%, mp $242\text{--}244^\circ\text{C}$. $^1\text{H NMR}$ (CDCl₃, ppm): δ 1.04 (t, $J = 6.8$ Hz, $-\text{CH}_2\text{CH}_3$, 3 H), 3.28 (q, $J = 6.8$ Hz, $-\text{CH}_2\text{CH}_3$, 2 H), 3.63 (t, $J = 4.8$ Hz, $-\text{CH}_2\text{CH}_2\text{O}-$, 2 H), 4.20 (t, $J = 4.8$ Hz, $-\text{CH}_2\text{CH}_2\text{O}-$, 2 H), 6.55 (d, $J = 8.5$ Hz, ArH, 2 H), 7.01 (d, $J = 3.5$ Hz, thienyl proton, 1 H), 7.15 (s, ArH, 1 H), 7.21 (m, ArH, 3 H), 7.33

(d, $J = 8.2$ Hz, ArH, 1 H), 7.35 (d, $J = 3.7$ Hz, thienyl proton, 1 H), 7.65 (m, ArH, 4 H), 7.74 (m, ArH, 2 H), 7.83 (m, ArH, 2 H), 7.90 (m, ArH, 2 H), 8.17 (d, $J = 8.6$ Hz, ArH, 2 H). Anal. Calcd for $C_{42}H_{30}N_4O_7S$: C, 68.65; H, 4.12; N, 7.62; S, 4.36. Found: C, 68.74; H, 4.10; N, 7.70; S, 4.45.

Compound 4b: 81%, mp 243–244 °C. 1H NMR ($CDCl_3$, ppm): δ 1.03 (t, $J = 6.9$ Hz, $-CH_2CH_3$, 3 H), 3.28 (q, $J = 6.9$ Hz, $-CH_2CH_3$, 2 H), 3.63 (t, $J = 5.6$ Hz, $-CH_2CH_2O-$, 2 H), 4.20 (t, $J = 5.7$ Hz, $-CH_2CH_2O-$, 2 H), 6.54 (d, $J = 8.7$ Hz, ArH, 2 H), 6.73 (d, $J = 16.0$ Hz, $-CH=CH-$, 1 H), 6.99 (d, $J = 16.3$ Hz, $-CH=CH-$, 1 H), 7.14 (d, $J_{12} = 1.6$ Hz, ArH, 1 H), 7.15 (d, $J = 8.8$ Hz, ArH, 2 H), 7.20 (dd, $J_{12} = 1.8$ Hz, $J_{23} = 8.8$ Hz, ArH, 1 H), 7.33 (d, $J_{23} = 8.7$ Hz, ArH, 1 H), 7.48 (d, $J = 8.7$ Hz, ArH, 2 H), 7.73 (m, ArH, 4 H), 7.86 (m, ArH, 2 H), 7.90 (m, ArH, 2 H), 8.12 (d, $J = 8.7$ Hz, ArH, 2 H). Anal. Calcd for $C_{40}H_{30}N_4O_7$: C, 70.79; H, 4.46; N, 8.26. Found: C, 70.53; H, 4.58; N, 8.33.

Compound 4c: 76%, mp 269–270 °C. 1H NMR ($CDCl_3$, ppm): δ 1.09 (t, $J = 7.0$ Hz, $-CH_2CH_3$, 3 H), 3.37 (q, $J = 7.0$ Hz, $-CH_2CH_3$, 2 H), 3.72 (t, $J = 5.4$ Hz, $-CH_2CH_2O-$, 2 H), 4.25 (t, $J = 5.4$ Hz, $-CH_2CH_2O-$, 2 H), 6.62 (d, $J = 9.0$ Hz, ArH, 2 H), 7.18 (d, $J_{12} = 1.7$ Hz, ArH, 1 H), 7.20 (d, $J_{12} = 1.7$ Hz, $J_{23} = 8.0$ Hz, ArH, 1 H), 7.33 (d, $J_{23} = 8.3$ Hz, ArH, 1 H), 7.58 (d, $J = 9.0$ Hz, ArH, 2 H), 7.63 (m, ArH, 2 H), 7.74 (m, ArH, 2 H), 7.80 (m, ArH, 2 H), 7.85 (d, $J = 8.9$ Hz, ArH, 2 H), 7.90 (m, ArH, 2 H), 8.28 (d, $J = 8.9$ Hz, ArH, 2 H). Anal. Calcd for $C_{38}H_{28}N_6O_7$: C, 67.05; H, 4.14; N, 12.35. Found: C, 67.09; H, 4.15; N, 12.29.

Compound 5. A general procedure for the syntheses of compounds **5a**, **5b**, and **5c** is described here. In a 50-mL three-necked flask equipped with a condenser and an addition funnel, compound **4** (0.4 mmol) and 20 mL of THF were mixed and heated to reflux. The hydrazine monohydrate (2.7 mL) in 5 mL of THF was added dropwise and the reaction solution became clear after the completion of the addition. After refluxing the solution for 2 h, the reaction flask was cooled down and the organic layer was separated from the water layer. The organic solution was then concentrated to the minimum amount. The white solid precipitated out of the solution was removed by filtration. The solvent was then removed from the filtrate and the red solid was recrystallized from chloroform/methanol under nitrogen.

Compound 5a: 83%, mp 165–167 °C. 1H NMR ($CDCl_3$, ppm): δ 1.23 (t, $J = 7.0$ Hz, $-CH_2CH_3$, 3 H), 3.31 (s, $ArNH_2$, 4 H), 3.49 (q, $J = 7.0$ Hz, $-CH_2CH_3$, 2 H), 3.77 (t, $J = 6.0$ Hz, $-CH_2CH_2O-$, 2 H), 4.10 (t, $J = 6.0$ Hz, $-CH_2CH_2O-$, 2 H), 6.16 (dd, $J_{12} = 1.9$ Hz, $J_{23} = 8.0$ Hz, ArH, 1 H), 6.20 (d, $J_{12} = 1.9$ Hz, ArH, 1 H), 6.52 (d, $J_{23} = 8.0$ Hz, ArH, 1 H), 6.74 (d, $J = 8.8$ Hz, ArH, 2 H), 7.13 (d, $J = 3.7$ Hz, thienyl proton, 1 H), 7.37 (d, $J = 3.7$ Hz, thienyl proton, 1 H), 7.46 (d, $J = 8.6$ Hz, ArH, 2 H), 7.66 (d, $J = 8.7$ Hz, ArH, 2 H), 8.16 (d, $J = 8.7$ Hz, ArH, 2 H). Anal. Calcd for $C_{26}H_{26}N_4O_3S$: C, 65.80; H, 5.52; N, 11.81; S, 6.76. Found: C, 65.74; H, 5.55; N, 11.74; S, 6.82.

Compound 5b: 82%, mp 182–184 °C. 1H NMR ($CDCl_3$, ppm): δ 1.23 (t, $J = 7.0$ Hz, $-CH_2CH_3$, 3 H), 3.34 (s, $ArNH_2$, 4 H), 3.52 (q, $J = 7.0$ Hz, $-CH_2CH_3$, 2 H), 3.80 (t, $J = 5.9$ Hz, $-CH_2CH_2O-$, 2 H), 4.13 (t, $J = 6.0$ Hz, $-CH_2CH_2O-$, 2 H), 6.20 (dd, $J_{12} = 2.4$ Hz, $J_{23} = 8.1$ Hz, ArH, 1 H), 6.24 (d, $J_{12} = 2.4$ Hz, ArH, 1 H), 6.57 (d, $J_{23} = 8.0$ Hz, ArH, 1 H), 6.77 (d, $J = 8.8$ Hz, ArH, 2 H), 6.92 (d, $J = 16.2$ Hz, $-CH=CH-$, 1 H), 7.20 (d, $J = 16.2$ Hz, $-CH=CH-$, 1 H), 7.44 (d, $J = 8.9$ Hz, ArH, 2 H), 7.56 (d, $J = 8.8$ Hz, ArH, 2 H), 8.18 (d, $J = 8.9$ Hz, ArH, 2 H). Anal. Calcd for $C_{24}H_{26}N_4O_3$: C, 68.88; H, 6.26; N, 13.39. Found: C, 68.93; H, 6.32; N, 13.37.

Compound 5c: 90%, mp 178–180 °C. 1H NMR ($CDCl_3$, ppm): δ 1.28 (t, $J = 7.0$ Hz, $-CH_2CH_3$, 3 H), 3.32 (s, $ArNH_2$, 4 H), 3.58 (q, $J = 7.0$ Hz, $-CH_2CH_3$, 2 H), 3.86 (t, $J = 5.3$ Hz, $-CH_2CH_2O-$, 2 H), 4.15 (t, $J = 5.2$ Hz, $-CH_2CH_2O-$, 2 H), 6.18 (d, $J = 8.0$ Hz, ArH, 1 H), 6.20 (s, ArH, 1 H), 6.52 (d, $J = 8.0$ Hz, ArH, 1 H), 6.81 (d, $J = 9.1$ Hz, ArH, 2 H), 7.87 (m, ArH, 4 H), 8.27 (d, $J = 9.0$ Hz, ArH, 2 H). Anal. Calcd for $C_{22}H_{24}N_6O_3$: C, 62.84; H, 5.75; N, 19.99. Found: C, 62.78; H, 5.81; N, 19.89.

Polymerization. A general polymerization procedure is described here. The diamino monomer **5** (0.415 mmol) was dissolved in 20 mL of anhydrous NMP at 0 °C, followed by the addition of the dianhydride monomer (0.415 mmol) at once. After the solution was stirred for 1 h and left at room temperature for 1 h, the resulting poly(amic acid) was processed either by further imidization using acetic anhydride and

pyridine mixture or by direct precipitation into methanol to give the solid poly(amic acid). The soluble polyimides were synthesized by chemical approach. The mixture of acetic anhydride and pyridine (8 mL/4 mL, 2 : 1) was added to the poly(amic acid) solution at room temperature and this mixture was stirred for 2 h and then heated to 90 °C for another 3 h. The polymer was precipitated into methanol (50 mL) and collected by filtration. The solid was further purified by dissolving it in THF and reprecipitated it into methanol. The polymer collected was washed with methanol in a Soxhlet extractor for 2 days and then dried under vacuum at 60 °C for 2 days.

Polyimides **4** and **5** were prepared by thermal approach. The solid poly(amic acid) was dissolved in polar aprotic solvents. Thin films were prepared from the solution and then cured at elevated temperature (220 °C) for 2 to 5 h to form the corresponding polyimide.

Polyimide 1. 1H NMR ($CDCl_3$, ppm): δ 0.99 (s, $-CH_2CH_3$, 3 H), 3.24 (s, $-CH_2CH_3$, 2 H), 3.61 (s, $-CH_2CH_2O-$, 2 H), 4.17 (s, $-CH_2CH_2O-$, 2 H), 6.53 (s, ArH, 2 H), 7.01 (s, thienyl proton, 1 H), 7.13 (s, ArH, 1 H), 7.17 (s, ArH, 1 H), 7.28 (s, ArH, 2 H), 7.32 (s, thienyl proton, 1 H), 7.57 (s, ArH, 2 H), 7.88 (m, ArH, 6 H), 8.07 (s, ArH, 2 H). Anal. Calcd for $C_{45}H_{28}F_6N_4O_7S$: C, 61.23; H, 3.20; N, 6.35; S, 3.63. Found: C, 61.25; H, 3.17; N, 6.39; S, 3.70.

Polyimide 2. 1H NMR ($CDCl_3$, ppm): δ 1.00 (s, $-CH_2CH_3$, 3 H), 3.25 (s, $-CH_2CH_3$, 2 H), 3.63 (s, $-CH_2CH_2O-$, 2 H), 4.18 (s, $-CH_2CH_2O-$, 2 H), 6.54 (d, $J = 7.8$ Hz, ArH, 2 H), 6.77 (d, $J = 15.8$ Hz, $-CH=CH-$, 1 H), 7.02 (d, $J = 15.8$ Hz, $-CH=CH-$, 1 H), 7.13 (s, ArH, 1 H), 7.21 (m, ArH, 2 H), 7.34 (d, $J = 7.1$ Hz, ArH, 1 H), 7.43 (d, $J = 6.0$ Hz, ArH, 2 H), 7.86 (m, ArH, 4 H), 7.96 (m, ArH, 2 H), 8.05 (s, ArH, 2 H). Anal. Calcd for $C_{43}H_{28}F_6N_4O_7$: C, 62.47; H, 3.41; N, 6.78. Found: C, 61.80; H, 3.55; N, 6.56.

Polyimide 3. 1H NMR ($CDCl_3$, ppm): δ 1.06 (s, $-CH_2CH_3$, 3 H), 3.34 (s, $-CH_2CH_3$, 2 H), 3.71 (s, $-CH_2CH_2O-$, 2 H), 4.23 (s, $-CH_2CH_2O-$, 2 H), 6.62 (s, ArH, 2 H), 7.16 (s, ArH, 1 H), 7.19 (s, ArH, 1 H), 7.34 (s, ArH, 1 H), 7.67 (s, ArH, 2 H), 7.90 (m, ArH), 8.19 (s, ArH, 2 H). Anal. Calcd for $C_{41}H_{26}F_6N_6O_7$: C, 59.43; H, 3.16; N, 10.14. Found: C, 58.54; H, 3.28; N, 10.03.

Polyimide 4. 1H NMR ($DMSO-d_6$, ppm): δ 1.12 (s, $-CH_2CH_3$, 3 H), 3.60 (s, $-CH_2CH_3$, 2 H), 3.89 (s, $-CH_2CH_2O-$, 2 H), 4.17 (s, $-CH_2CH_2O-$, 2 H), 6.87 (s, ArH, 2 H), 7.20 (s, ArH, 1 H), 7.70 (m, ArH), 8.23 (s, ArH, 2 H), 9.50 (s, $-NHCO-$, 1 H), 10.50 (s, $-NHCO-$, 1 H), 13.3 (s, $-COOH$, 2 H). Anal. Calcd for $C_{32}H_{26}N_6O_9$: C, 60.19; H, 4.10; N, 13.16. Found: C, 58.37; H, 4.41; N, 12.64.

Polyimide 5. 1H NMR ($CDCl_3$, ppm): δ 1.12 (s, $-CH_2CH_3$, 3 H), 3.52 (s, $-CH_2CH_3$, 2 H), 3.86 (s, $-CH_2CH_2O-$, 2 H), 4.17 (s, $-CH_2CH_2O-$, 2 H), 6.82 (s, ArH, 2 H), 7.17 (s, ArH, 1 H), 7.70 (m, ArH), 8.23 (s, ArH, 2 H), 9.30 (s, $-NHCO-$, 1 H), 10.50 (s, $-NHCO-$, 1 H), 13.3 (s, $-COOH$, 2 H). Anal. Calcd for $C_{39}H_{30}N_6O_{10}$: C, 63.07; H, 4.07; N, 11.32. Found: C, 60.99; H, 4.31; N, 10.28.

The 1H NMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. The FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer. A Perkin Elmer Lambda 6 UV/vis spectrophotometer was used to record the UV/vis spectra. Thermal analyses were performed by using the DSC-10 and TGA-50 systems from TA instruments under a nitrogen atmosphere. The melting points were obtained with open capillary tubes on a Mel-Temp apparatus. Elemental analyses were performed by Atlantic Microlab, Inc. The refractive indices of the polyimides were measured by using a Metricon Model 2010 prism coupler.

The second-order NLO activities of the corona poled polymer films were characterized by performing a second harmonic generation experiment. The poling conditions were as follows: temperature, 220 °C; voltage, 3 kV at the needle point; gap distance, 1 cm; poling current < 1 μ A. A Mode-Locked Nd:YAG laser (Continuum PY61C-10, 10-Hz repetition rate) was used as the light source. The second harmonic signal generated by the fundamental wave (1064 nm) was detected by a photomultiplier tube (PMT). After amplification it was averaged in a boxcar integrator. A quartz crystal was used as the reference sample.

An electro-optic coefficient (r_{33}) was determined by the simple reflection technique.¹⁶ A polymer film with a thickness of 2–3 μ m was prepared by casting a tetrachloroethane (TCE) solution of polymer onto an indium–tin oxide (ITO) glass. After corona poling, a silver electrode of 700 Å was deposited on the polymer film by vacuum

evaporation. A He-Ne laser (632.8 nm) and a diode laser (780 nm) were used as the light sources.

Results and Discussion

Synthesis of Monomers. Our approach to the synthesis of functionalized polyimides began with the synthesis of nonlinear optical chromophores bearing the diamino moieties. In order to keep the functional groups in the chromophore (such as nitro, azo moieties) intact, mild reaction conditions are required. We found that the Mitsunobu reaction can be utilized to achieve the goal. It is known that the Mitsunobu reaction effects occur at room temperature and usually give a high yield to the alkylation of phenols.¹³ The treatment of compounds **2** and **3** with the diethyl azodicarboxylate/triphenylphosphine in *N*-methylpyrrolidinone afforded diimido compound **4** in ca. 80% yield (Scheme 1). The hydrazinolysis of diimido compounds yielded the corresponding diamino monomers (see Scheme 1). In this paper, we present the results of polyimides functionalized with three NLO chromophores. These NLO chromophores are the push-pull type compounds (compound **3** in Scheme 1) with an amino group as the electron donor and the nitro group as the electron acceptor linked by conjugated moieties. The difference among them is that they possess a different linking moiety X, hence, different $\mu\beta$ values and thermal stability. The $\mu\beta$ value of chromophore **3c** (disperse red 1) is 343×10^{-48} esu and that of chromophore **3b** (DANS) is 482×10^{-48} esu.^{14a} The diaryl thiophene chromophore **3a** has a value which is ca. 60% of that of DANS.^{14b} However, the thermal stability observed in TGA measurements for chromophore **3a** is better than that for both **3b** and **3c**: the decomposition temperature (T_d , the onset temperature measured in TGA) is 312, 277, and 264 °C for **3a**, **3b**, and **3c**, respectively. The absorption peaks for **3a**, **3b**, and **3c** are at 445, 440, and 480 nm, respectively.

The synthetic procedures of these push-pull chromophores are known. Scheme 2 outlines the approach for the synthesis of compound **3a**, which is a modified literature approach.¹⁵ The diaryl thiophene chromophore was synthesized by consecutive palladium-catalyzed cross-coupling reactions of aromatic organozinc reagents and aromatic halides. The 2-thienylzinc chloride was prepared by treating the corresponding Grignard reagent made from 2-bromothiophene with anhydrous zinc(II) chloride. This approach can be used as a general way to synthesize the aryl thiophene compounds by a stepwise construction.

Synthesis and Characterization of Polyimides. The polymerization procedure consists of two steps: (1) the polymerization of a diamino monomer with a dianhydride monomer, yielding the poly(amic acid), (2) the imidization of the poly(amic acid) either by chemical cyclization or thermal cyclization (Scheme 3). The 1-methyl-2-pyrrolidinone (NMP) was used as the solvent for the polymerization; other aprotic solvents, such as *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF), are also suitable for the purpose of polymerization. The chemical imidization was effected by adding a mixture of pyridine and acetic anhydride to the NMP solution of poly(amic acid). For the thermal cyclization, a solution of the poly(amic acid) was cast or spin-coated onto glass substrate, which was then cured at elevated temperatures. The polyimides

Table 1. Molecular Weights or Intrinsic Viscosities of Polyimides and Poly(amic acid)s

polyimides	M_n	M_w	polydispersity	η_{int} , dL/g
polyimide 1	12 000	42 000	3.5	
polyimide 2	14 000	34 000	2.4	
polyimide 3	14 000	35 000	2.5	
polyimide 4				0.95
polyimide 5				0.34

synthesized by both approaches showed similar FTIR spectra. Due to the poor solubility in common solvents, polyimide films synthesized from pyromellitic dianhydride (PMDA) or benzophenone tetracarboxylic dianhydride (BTDA) are usually prepared from the corresponding poly(amic acid) films by using the thermal approach. The polyimides synthesized from hexafluoroisopropylidene diphthalic dianhydride followed by a chemical cyclization using pyridine and acetic anhydride are soluble in common organic solvents, such as chloroform, THF, DMF, DMSO, and NMP. The bulky hexafluoroisopropylidene moiety in the polyimide backbone reduced the intermolecular interaction and greatly enhanced the solubility. Soluble polyimides offer good processibility and optical quality thin films which can be easily prepared from their solutions.

The structures of the soluble polyimides **1–3** were characterized by different spectroscopic techniques. The ¹H NMR spectra show that there are four typical aliphatic peaks around 1.00, 3.30, 3.60, and 4.20 ppm due to the chemical shifts of the methyl and methylene protons connected with the amino group in the NLO chromophores. The chemical shifts in the NMR spectra of polyimides **1**, **2**, and **3** were assigned based on the comparison with those of corresponding model compounds **4a**, **4b**, and **4c**. For both polyimides **1** and **2**, the chemical shifts for the aromatic protons (two benzenoid) in the NLO chromophore moieties appear around 6.50, 7.20, 7.50, and 8.10 ppm. The corresponding chemical shifts for polyimide **3** appear at 6.60, 7.60, 7.90, and 8.20 ppm. For polyimide **1**, the chemical shifts of the two protons in the thiophene moiety appear at ca. 7.00 and 7.30 ppm. The two doublets were found at 6.80 and 7.00 ppm due to the chemical shifts of the two protons of the double bond in the stilbene in polyimide **2**. Because polyimides **4** and **5** are insoluble, only the NMR spectra of poly(amic acid)s can be taken using polar solvents like DMSO. The poly(amic acid)s have three characteristic downfield peaks at ca. 13.3, 10.5, and 9.5 ppm in NMR spectra which are the chemical shifts of protons in the carboxylic acid and amide groups.

In FTIR spectra, the polyimides have characteristic absorption peaks at ca. 1780 and 1728 cm⁻¹, attributed to the imide rings which do not appear in the spectra of poly(amic acid)s. All the soluble polyimides have these two absorption peaks. In regard to the insoluble polyimides, the poly(amic acid)s have two strong absorption peaks around 1720 cm⁻¹ for amide carbonyl groups and 1670 cm⁻¹ for carboxylic carbonyl groups before imidization. During the thermal imidization process, these peaks greatly decreased and simultaneously the two characteristic peaks of the polyimides appeared.

The results of the UV/vis study of these polyimides are shown in Table 1. After the molecular dipoles were aligned along the direction of the high electric field, the maximum absorbances due to the chromophore moieties were reduced. At the same time the peaks were all slightly blue-shifted (see Figure 1). The order parameters ($\Phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after corona poling) are used to characterize the poling efficiency. Theoretically, the larger the order parameter, the better poled the polymers. A typical order parameter for polyimides is ca. 0.3 for soluble polyimides.

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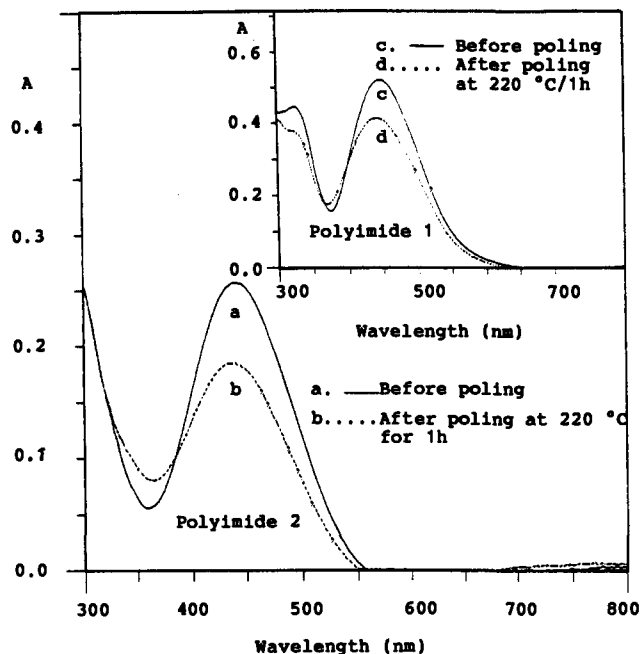


Figure 1. UV/vis spectra of polyimides 1 and 2 before and after electric poling.

Usually, the soluble polyimides are easier to pole than the insoluble ones.

For the soluble polyimides, the molecular weights were measured in THF using GPC (polystyrene as standard). The results are also shown in Table 1. For the insoluble polyimide, the molecular weight cannot be measured by GPC or viscosity. Instead, the viscosity of the poly(amic acid) is measured in NMP by a Ubbelohde type viscometer. The intrinsic viscosity was obtained by extrapolating to infinite dilution. The molecular weight measurement of polyimide 2 showed a weight-averaged molecular weight of 34k Daltons (polydispersity of 2.4). The measurement for polyimide 3 gave similar results. The weight-averaged molecular weight for polyimide 1 was 42k daltons with a broader molecular weight distribution (polydispersity of 3.5) than polyimides 1 and 2. The viscosity measurements using NMP as the solvent indicate that the poly(amic acid) of polyimide 4 has a much higher viscosity than that of polyimide 5, which implies that the former has a higher molecular weight.

Thermal properties of the polyimides were examined by TGA and DSC measurements. In the DSC study, the glass transition temperatures (T_g) of these insoluble polyimides were not observed before they decomposed (Figure 2), implying that T_g s could be higher than the decomposition temperatures (T_d). On the other hand, the soluble polyimides have T_g s around 230 °C and similar decomposition temperatures (T_d) around 320 °C. Polyimides 3, 4, and 5 have the same chromophore but different polyimide backbones (6FDA (3) vs PMDA (4) and BTDA (5)). The T_g s for the insoluble polyimides 4 and 5 cannot be observed in the DSC traces before the decomposition temperature, but polyimide 3 has a very clear T_g at 230 °C. The decomposition temperature for the soluble polyimide 3 (319 °C) is higher than those of the insoluble polyimides 4 and 5 (291 and 303 °C, see Figure 3). Before imidization, the poly(amic acid)s of polyimides 4 and 5 have an endothermic peak in the DSC trace, starting at ca. 180 °C and ending at ca. 220 °C. In the TGA, a small weight loss starting at 180 °C was observed corresponding to the dehydration of poly(amic acid)s in the imidization process. The weight loss of polyimides at 300 °C is caused by the decomposition of chromophores, judging from the TGA studies of NLO chromophores. It is known that the polyimide backbones decompose above 500 °C, which can be observed

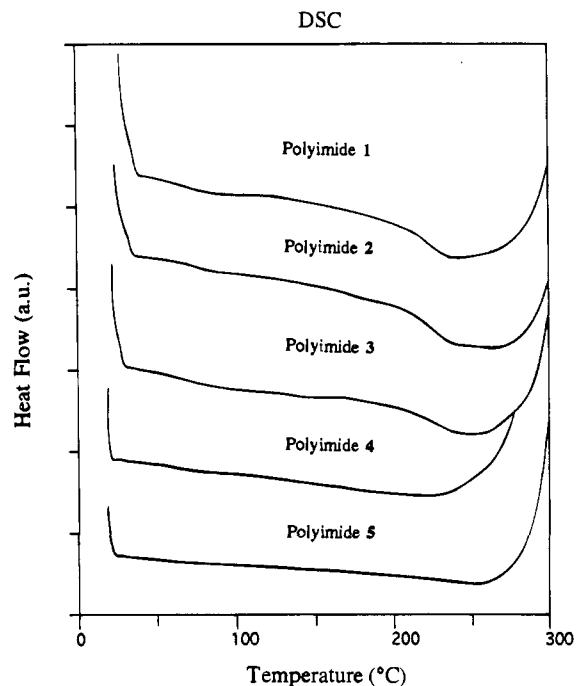


Figure 2. DSC diagrams of polyimides 1–5 with the heating rate of 10 °C/min under nitrogen atmosphere.

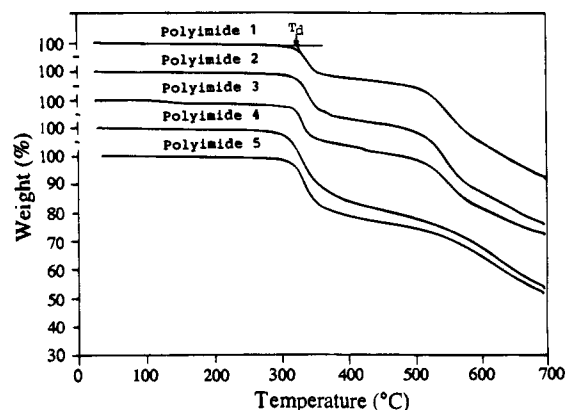


Figure 3. TGA traces of polyimides 1–5 with the heating rate of 10 °C/min under nitrogen atmosphere.

in TGA traces of polyimides (Figure 3). It suggests that the thermal properties of the NLO polyimide systems can be greatly enhanced if the NLO chromophores stable at high temperature are properly chosen.¹⁰

Nonlinear Optical Properties. The second-order nonlinear optical 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 close to the glass transition temperature so that the molecular dipole 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 2 lists the d_{33} values of these polyimides at the wavelength of 532 nm. It can be found that polyimide 3 exhibits the largest d_{33} value at 532 nm (169 pm/V). However, its nonresonant value deduced from the two-level approximate model is smaller than polyimide 2 and is close to polyimide 1.¹⁷ It is clear that a large resonant enhancement exists in polyimide 3, which is evident from the UV/vis spectra of the polymer. For those

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Table 2. Physical Properties of Polyimides

polyimides	d_{33}^a (532 nm, pm/V)	$d_{33}(\infty)$ (pm/V)	r_{33} (780 nm, pm/V)	λ_{\max} (nm)	T_g^b ($^{\circ}\text{C}$)	T_d^c ($^{\circ}\text{C}$)
polyimide 1	103	21	24	445	227	322
polyimide 2	146	40	46	440	229	321
polyimide 3	169	18	27	477	235	319
polyimide 4	69	9	7	470		291
polyimide 5	59	7	7	490		303

^a $d_{33}(\infty)$: nonresonant SHG coefficient estimated by the two-level model. ^b T_g : glass transition temperature. ^c T_d : decomposition temperature.

insoluble polyimides, much smaller d_{33} values were obtained although the chromophore densities of these polyimides are comparable with that of polyimide 3. The difference is caused by the difference in efficiency of corona poling since the decomposition temperatures of these polyimides are much higher than the poling temperatures and the chromophores were not damaged at the poling temperatures for polyimides 4 and 5. Since the T_g s of insoluble polyimides are not observable, the polymer thin films made from the corresponding poly(amic acid) solution have to be poled during the imidization process. The imidization temperatures of polyamic acids are approximately 180 $^{\circ}\text{C}$. After imidization, the dipole was fixed by the polyimide matrix. It seems to be true that the poling efficiency during imidization cannot be maximized and as soon as the temperature rises above 200 $^{\circ}\text{C}$ the glass transition temperature cannot be reached before the decomposition. Thus, the dipole orientation in polyimides 4 and 5 is not optimized and smaller d_{33} values were observed. This trend is consistent with the order parameter measurement results: Φ values of 0.14 and 0.16 were obtained for polyimides 4 and 5, respectively. The trends in r_{33} values of these polyimides are consistent with those of d_{33} values. Since measurements of the electro-optic coefficients at 780 nm are away from the absorption band in the UV/vis spectra and have little resonant enhancement, the highest r_{33} value (46 pm/V) was observed with polyimide 2. Polyimides 1 and 3 exhibit similar r_{33} values and polyimides 4 and 5 have much smaller r_{33} values (see Table 2).

Because the thermal relaxation process of the dipole orientation is directly related to the free volume in the polymer, a critical free volume is required for the relaxation of the orientation of the dipole. This critical free volume is related to the glass transition temperature; a high glass transition temperature (T_g) implies a higher orientational stability. An effective probe for this stability is to monitor the temporal and temperature stabilities of the second harmonic generation. At room temperature, all of the polyimides are stable and there is no decay in the intensity of the second harmonic generation signal. At 100 $^{\circ}\text{C}$ in air, after an initial decay to ca. 90% of the original signal, more than 80% of the SHG signal remained after 3000 h for polyimide 3 (see Figure 4). The SHG signals of all the polyimides remained significantly stable even at higher temperatures. For example, the initial signals only decayed by ca. 20% after 800 h at 150 $^{\circ}\text{C}$ in the air, as shown in Figure 5.

Temporal stability studies yield information on the decay of the SHG signal as a function of the time at a specific temperature, which is obviously a time-consuming experiment. Temperature-dependent SHG measurements yield information of the SHG stability as a function of temperature. Figure 6 shows such a result for polyimide 1, where the heating rate is 4 $^{\circ}\text{C}/\text{min}$ and the samples were exposed to the air during the whole measurement. The SHG signal was quite stable until the temperature reached 200 $^{\circ}\text{C}$ (for example, see Figure 6). A fast decay of the SHG signal was observed when the temperature was close to the polymer's glass transition temperature, ~ 227 $^{\circ}\text{C}$. The signal completely disappeared when the temperature was above the T_g . However, it was found that the same magnitude of the SHG signal can be recovered from this sample

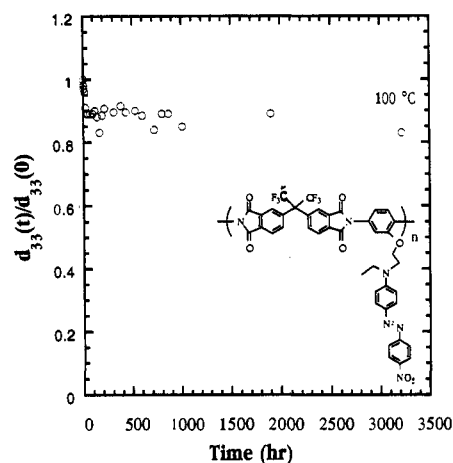


Figure 4. Temporal stability of the SHG signal of polyimide 3 at 100 $^{\circ}\text{C}$ in the air.

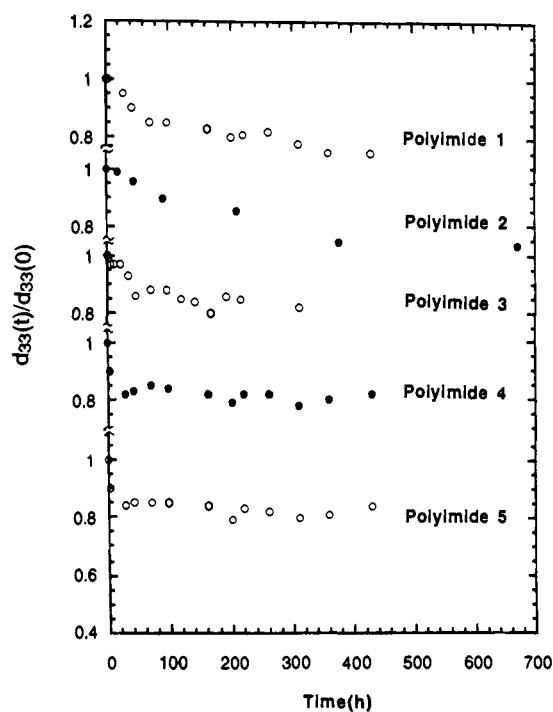


Figure 5. Temporal stability of the SHG signals of polyimides 1–5 at 150 $^{\circ}\text{C}$ in the air.

after it was repoled by corona discharging, indicating that the NLO chromophore was not damaged after experiencing high temperatures. Similar results were observed with polyimides 2 and 3. These thermal characteristics and their optical nonlinearities clearly indicate that these polymers are useful in device applications.

Another major issue in NLO polymers is their high optical loss. We have measured the optical loss in a few samples prepared in an ambient environment (without using a dust-free clean room). A reasonably small optical loss (2.0 dB/cm at 632 nm) was observed for unpoled polyimides at 632 nm which

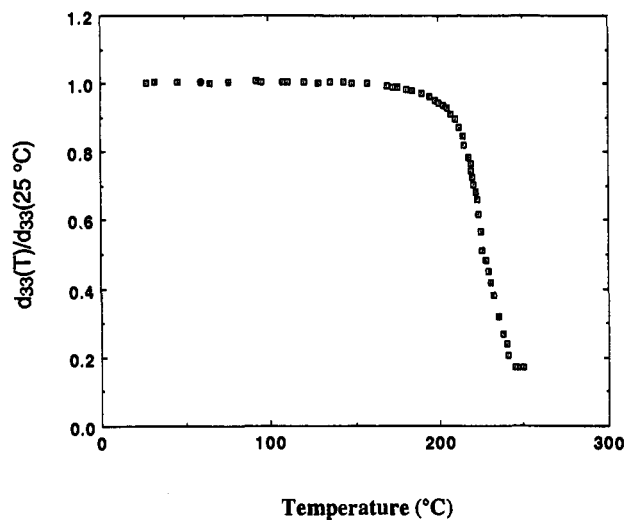


Figure 6. SHG signal of polyimide 1 as a function of temperature. implied that if the measurements were done with a thin film prepared in a dust-free environment and at a longer wavelength, a smaller optical loss may be expected. However, detailed

measurements are needed to obtain the true value in longer wavelengths.

Conclusions

A general approach to the synthesis of high-performance second-order nonlinear optical (NLO) polyimides is described. These polyimides are designed to address three issues in second-order NLO materials: the instability of the dipole orientation, inadequate optical nonlinearity, and high optical loss. Physical studies indicate that these polyimides exhibit long-term and high thermal stability in dipole orientation, relatively large electro-optic coefficients, and low optical losses. Although all of these properties are not optimized, the overall performance of these polyimides makes them very attractive for practical applications.

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