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Design and Synthesis of Functionalized Polyimides for Second-Order Nonlinear Optics

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ABSTRACT: A functionalized aromatic polyimide with a pendent nonlinear optical chromophore has been synthesized. The detailed characterization indicated very promising features for this polymer. The poly(amic acid) is soluble in several aprotic polar solvents, permitting thin film processing. The poly(amic acid) can be imidized at ca. 200 °C without damaging the NLO chromophore. A glass transition temperature of 240 °C was observed for the polyimide, which rendered a high stability of the optical nonlinearity at elevated temperatures. Long-term stability was observed at 170 °C.

Introduction

Interest in nonlinear optical (NLO) materials, both inorganic and organic, has grown tremendously in recent years, primarily because of their potential application in electro-optic devices.[1-3] It is known that organic NLO materials possess several advantages over inorganics, such as larger second-order susceptibilities, a higher laser damage threshold, and ease in processing and architectural modification for optimizing optical nonlinearities. Therefore, a great deal of research effort has been focused on organic materials, such as asymmetric organic single crystals, oriented polymers, and Langmuir–Blodgett films.[1-3] Among these, the oriented polymer systems are especially attractive for NLO studies because they possess good optical properties, wide variety, and low cost. However, in order to be useful in optical device applications, second-order NLO polymers should be chemically and physically stable. They should also maintain a significant bulk nonlinearity at elevated working temperatures that can reach 80 °C or higher and possible device processing temperatures of 200 °C. These practical considerations have led investigators to search for new polymeric systems which exhibit better temporal and thermal NLO stability.

Polyimides have been extensively studied as high-performance materials for applications in integrated electronic circuits and aerospace devices due to their exceptional thermal, mechanical, optical, and dielectric properties.[4,5] Recently, the unique properties of polyimides have aroused much attention from the optical community for their photonic applications.[6-8] The high glass transition temperatures of these materials have been utilized to prepare second-order nonlinear optical (NLO) composite materials which exhibit exceptionally high temperature stability in the dipole orientation. While these systems enjoyed a certain degree of success, several problems also occurred. For example, NLO chromophore bleaching was observed in polyimide composite systems, and the glass transition temperature decreased because of the plasticizing effect of the small chromophore at prolonged high working temperatures, and so on. These problems severely hindered further development of these materials for practical applications.

In our previous work, we have succeeded in synthesizing a functionalized second-order NLO aliphatic polyimide which exhibits exceptional thermal stability and temporal stability of the second harmonic generation (SHG) signal.[9] However, aromatic polyimides possess higher glass transition temperatures (T_g), higher temperature resistance, and greater structural versatility.[4,5] It will be very interesting to synthesize these polyimides which are functionalized by a NLO chromophore. But so far, there are no aromatic polyimides functionalized with a NLO chromophore being synthesized. This is partially due to the difficulty of their synthesis. In this paper, we report the detailed studies of such a polymer.

Experimental Section

THF was purified by distillation over sodium chips and benzophenone. *N*-Methylpyridine (NMP) and dimethylformamide (DMF) was purified by distillation over phosphorus pentoxide. 1,2,4,5-Benzenetetracarboxylic dianhydride (monomer B) was purified by recrystallization from acetic anhydride and dried under a vacuum at 150 °C overnight. All of the other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated. The synthesis of the monomer and polymers is shown in Scheme 1.

4-[*N*-Ethyl-*N*-[benzoyloxy)ethyl]amino]benzaldehyde. DMF (30 mL) was cooled to 0 °C and treated dropwise with phosphorus oxychloride (17 mL, 0.17 mol). The resulting orange solution was stirred sequentially at 0 °C for 1 h and 25 °C for another 1 h. *N*-Ethyl-*N*-[(benzoyloxy)ethyl]aniline[10,11] (45.5 g) was added dropwise, and the mixture was heated at 90 °C for 6 h. After being cooled down to room temperature, the solution was poured into ice-cold water. The mixture was neutralized with a saturated sodium acetate solution and then extracted with dichloromethane (3 × 25 mL). The combined organic layer was washed with water (2 × 25 mL) and then with a saturated sodium chloride solution (25 mL). After the removal of the solvent, the crude product was chromatographed using CH_2Cl_2/MeOH (100:1) as the eluent, yielding an orange liquid (32.2 g, 64%). ^{1}H NMR ($CDCl_3$, ppm): δ 1.24 (t, J = 7.1 Hz, $-\mathrm{CH_2}\mathit{CH}_3$, 3 H), 3.53 (q, J = 7.1 Hz, $-\mathit{CH}_2\mathrm{CH_3}$, 2 H), 3.76 (t, J = 6.2 Hz, $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{N}-$, 2 H), 4.48 (t, J = 6.2 Hz, $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2N}-$, 2 H), 6.76 (d, J = 8.8 Hz, ArH, 2 H), 7.38 (t, J = 7.7 Hz, ArH, 2 H), 7.51 (t, J = 7.4 Hz, ArH, 1 H), 7.69 (d, J = 8.8 Hz, ArH, 2 H), 7.95 (d, J = 7.5 Hz, ArH, 2 H), 9.67 (s, ArCHO, 1 H).

4-[*N*-Ethyl-*N*-(β-hydroxyethyl)amino]-4′-(methylsulfonyl)stilbene (compound 2).[10,11] To a dried, three-necked, 250-mL round-bottom flask were added 1,2-dimethoxyethane (20 mL) and sodium hydride (1.9 g, 0.08 mol) under nitrogen. The mixture was stirred for 5 min, and 4-[*N*-ethyl-*N*-[(benzoyloxy)ethyl]amino]benzaldehyde (16.0 g, 0.05 mol) in 1,2-dimethoxyethane (20 mL) was then added. Diethyl(4-methylsulfonyl)benzyl phosphonate[12] (16.5 g, 0.05 mol) in 1,2-dimethoxyethane (20 mL) was added slowly. The solution was heated to reflux for 8 h and then poured into the crushed ice (80 g) under nitrogen. The

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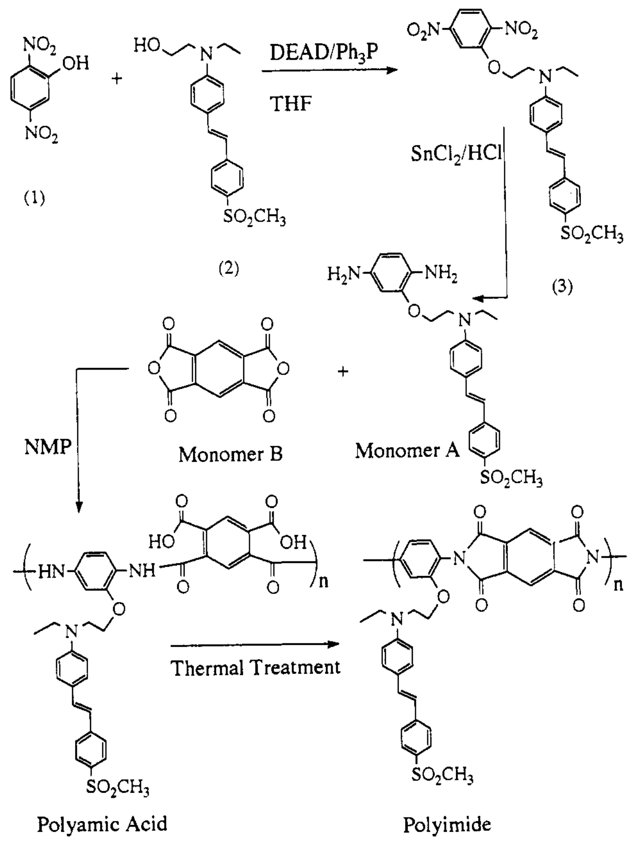
Scheme 1. Synthesis of monomer A, Poly(amic Acid), and Polyimide



mixture was extracted with dichloromethane (3 × 20 mL). The organic layer was washed with water (3 × 20 mL). After removal of the solvent, the crude product was hydrolyzed by sodium hydroxide solution (10%) to yield a yellow solid which was recrystallized from chloroform/hexane (10 g, 58%, mp 175–176 °C). ^1H NMR ($CDCl_3$, ppm): δ 1.18 (t, J = 7.0 Hz, $-CH_2CH_3$, 3 H), 3.03 (s, $-SO_2CH_3$, 3 H), 3.45 (q, J = 7.0 Hz, $-CH_2CH_3$, 2 H), 3.50 (t, J = 5.6 Hz, $-OCH_2CH_2N-$, 2 H), 3.80 (t, J = 5.6 Hz, $-OCH_2CH_2N-$, 2 H), 6.71 (d, J = 8.6 Hz, ArH, 2 H), 6.86 (d, J = 16.2 Hz, =CH, 1 H), 7.12 (d, J = 16.2 Hz, =CH, 1 H), 7.36 (d, J = 8.6 Hz, ArH, 2 H), 7.56 (d, J = 8.3 Hz, ArH, 2 H), 7.81 (d, J = 8.3 Hz, ArH, 2 H). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 65.68; H, 6.84; N, 4.03.

Compound 3. Diethyl azodicarboxylate (DEAD; 1.20 g, 6.9 mmol) in THF (5 mL) was added dropwise to the mixture of compound **2** (1.83 g, 5.3 mmol), 2,5-dinitrophenol (0.78 g, 5.3 mmol), and triphenylphosphine (1.81 g, 6.9 mmol) in 35 mL of THF at room temperature. After the reaction mixture was stirred for 24 h, water (50 mL) was added. The resulting solid was collected by filtration and recrystallized from acetone/methanol to yield dark black crystals (2.30 g, 85%, mp 176–177 °C). ^1H NMR ($CDCl_3$, ppm): δ 1.22 (t, J = 6.9 Hz, $-CH_2CH_3$, 3 H), 3.04 (s, $-SO_2CH_3$, 3 H), 3.52 (q, J = 7.0 Hz, $-CH_2CH_3$, 2 H), 3.86 (t, J = 5.2 Hz, $-OCH_2CH_2N-$, 2 H), 4.36 (t, J = 5.2 Hz, $-OCH_2CH_2N-$, 2 H), 6.68 (d, J = 8.6 Hz, ArH, 2 H), 6.87 (d, J = 16.2 Hz, =CH, 1 H), 7.13 (d, J = 16.2 Hz, =CH, 1 H), 7.39 (d, J = 8.5 Hz, ArH, 2 H), 7.56 (d, J = 8.1 Hz, ArH, 2 H), 7.82 (d, J = 8.3 Hz, ArH, 2 H), 7.87 (m, ArH, 3 H). Anal. Calcd for $C_{25}H_{25}N_3O_7S$: C, 58.71; H, 4.89; N, 8.22. Found: C, 58.63; H, 4.96; N, 8.18.

Monomer A. Stannous chloride (3.71 g, 19.6 mmol) was added to compound **3** (1.0 g, 2.0 mmol) in 50 mL of hydrochloric acid (36.5–38%). The mixture was stirred at room temperature for 24 h and then warmed to 40–50 °C for 2 h until the solution become completely transparent. Deoxygenated sodium hydroxide solution (40%) was then added to the mixture at an ice bath until the pH value of the solution reached 12–13. A yellow solid was collected by filtration under nitrogen and then recrystallized from $MeOH/H_2O$ to yield a bright yellow crystals (0.5 g, 57%, mp 166–168 °C). ^1H NMR ($CDCl_3$, ppm): δ 1.22 (t, J = 6.9 Hz, $-CH_2CH_3$, 3 H), 3.03 (s, $-SO_2CH_3$, 3 H), 3.30 (br s, $ArNH_2$ 4 H), 3.48 (q, J = 7.0 Hz, $-CH_2CH_3$, 2 H), 3.77 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2 H), 4.09 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2 H), 6.16 (d, J = 8.2 Hz, ArH, 1 H), 6.19 (s, ArH, 1 H), 6.51 (d, J = 8.1 Hz, ArH, 1 H), 6.72 (d, J = 8.6 Hz, ArH, 2 H), 6.86 (d, J = 16.2 Hz, =CH, 1 H), 7.12 (d, J = 16.2 Hz, =CH, 1 H, 7.37 (d, J = 8.3 Hz, ArH, 2 H), 7.56 (d, J = 8.1 Hz, ArH, 2 H), 7.81 (d, J = 8.0 Hz, ArH, 2 H). Anal. Calcd for $C_{25}H_{29}N_3O_3S$: C, 66.52; H, 6.43; N, 9.31. Found: C, 66.67; H, 6.49; N, 9.16.

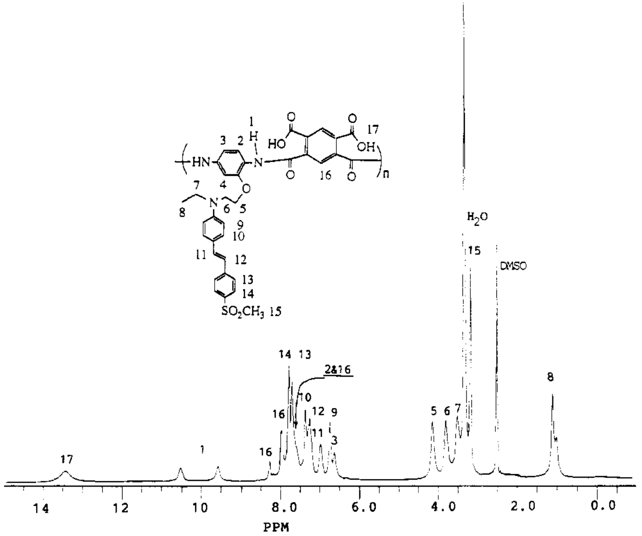


Figure 1. ^1H NMR spectrum of the poly(amic acid).

Polymerization. The pyromellitic dianhydride (PMDA; 0.060 g, 0.275 mmol) was added into a 25-mL two-necked, round-bottom flask containing monomer A (0.124 g, 0.275 mmol) and distilled NMP (10 mL) at −2 to −5 °C under nitrogen. The dianhydride was completely dissolved in ca. 20 min. The mixture was stirred between −2 and −5 °C for 4 h after the addition. The poly(atomic acid) was precipitated into methanol and collected by filtration (almost quantitative yield). To purify the polymer, it was ground in acetone to removal the residual solvent and then washed with chloroform in a Soxhlet extractor for 2 days. The ^1H NMR (DMSO, ppm) spectrum is shown in Figure 1. Anal. Calcd for $C_{35}H_{31}N_3O_9S$: C, 62.78; H, 4.63; N, 6.28. Found: C, 62.61; H, 4.38; N, 6.14.

Characterization. The ^1H NMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. 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 NMP solution of the poly(amic acid) was filtered through 0.2-μm syringe filters and then spin cast onto indium–tin oxide (ITO) coated glass slides or normal glass slides. The films were dried in an oven at 40 °C for 48 h under nitrogen and then at 60 °C overnight under vacuum. The films were poled/cured at a corona-discharge setup with a tip-to-plane distance of 1.0 cm at elevated temperatures from 60 to 200 °C within 2 h. The second-order NLO properties of poled polymeric films were characterized by second harmonic generation (SHG) measurements. A mode-locked Nd:YAG laser (continuum-PY61C-10, 25 ps, 10-Hz repetition rate) was used as a fundamental light source (1064 μm). The second harmonic signal was detected and amplified by a photomultiplier tube (PMT) and then averaged in a boxcar integrator. The temporal stability of the SHG signal of the polyimide was monitored at the following temperatures: room temperature and 90, 150, and 170 °C, respectively. The temperature reading error is within ±5 °C. Detailed descriptions of the measurements are given in ref 13.

Results and Discussion

Our strategy in synthesizing the functionalized polyimides was to functionalize the diamine monomers. The

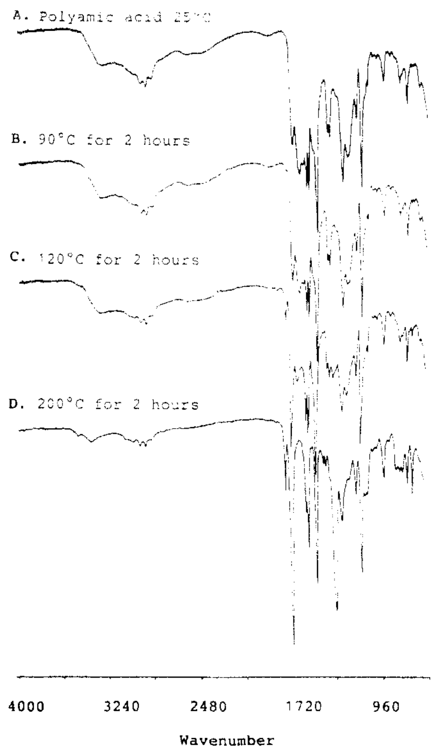


Figure 2. FTIR spectra of the polymer at various temperatures: (A) poly(amic acid) at room temperature; (B) 90 °C for 2 h; (C) 120 °C for 2 h; (D) 200 °C for 2 h.

key step in the synthesis was to utilize the Mitsunobu reaction to attach the NLO chromophore to 2,5-dinitrophenol (see Scheme 1). The reaction went smoothly, and the yield was high. Compound 3 was further reduced using $SnCl_2$ in a concentrated hydrochloric acid solution at room temperature. Here, we took the advantage that the sulfonyl group in the NLO chromophore is not sensitive to $SnCl_2$. The monomer obtained was very easy to purify. Both spectroscopic and microanalysis results supported the structure as proposed.

Polymerization can be effected easily in aprotic polar solvents (such as DMAC, NMP, etc.). The poly(amic acid) solution can be directly used to prepare films or can be precipitated into acetone to obtain solid materials. The poly(amic acid) was a yellow solid and soluble in aprotic polar solvents such as NMP, DMSO, and DMF. Viscosity measurements indicated an intrinsic viscosity of 0.58 dL/g. Optical quality films were cast from these solutions for further studies.

The structure of the poly(amic acid) was characterized by spectroscopic methods. The ^1H NMR spectrum of the poly(amic acid) is shown in Figure 1. The spectral assignments clearly support the structure as proposed. For example, the chemical shifts due to the NLO chromophore are similar to those in the monomer (peaks 5–15; the labeling was shown in the structural formula of the poly(amic acid)). Two peaks at 9.6 and 10.5 ppm can be ascribed to the amide protons. The chemical shift due to the carboxylic acid protons appeared at 13.4 ppm. The proton 16 should exhibit three chemical shifts due to cis and trans amidization. Two of them can be identified at 8.0 and 8.3 ppm, and the other one is overlapped with peaks around 7.5 ppm. The chemical shifts of protons 2, 3, and 4 are also overlapped with others except for one at 6.6 ppm which can be ascribed to proton 3.

FTIR spectra of the poly(amic acid) (Figure 2, curve A) exhibited a typical amide carbonyl absorption at 1720 cm^{-1} and a carboxylic carbonyl absorption at 1670 cm^{-1}. A medium absorption due to *trans*-stilbene in the NLO chromophore can be identified at 958 cm^{-1}. After the poly(amic acid) was thermally treated at different temperatures, imidization occurred. When the poly(amic acid) was annealed at 90 °C for 2 h, very little change was observed. A small peak at 1780 cm^{-1}, typical imide ring absorption, appeared. If the sample was annealed at 120 °C for 2 h, the absorption of the imide structure at 1780 and 725 cm^{-1} became stronger. If the sample was annealed at 200 °C for 2 h, the sample was fully imidized as evidenced by the appearance of strong absorption peaks at 1780 and 725 cm^{-1} and the disappearance of carboxylic carbonyl absorption at 1670 cm^{-1}. Simultaneously, the carbonyl absorption at 1720 cm^{-1} on rings became much stronger, while the absorption at 958 cm^{-1} due to the stilbene trans double bond did not change appreciably. The results indicated the curing process did not damage the NLO chromophore. This indication was further supported by the UV/vis spectroscopic studies and by TGA and DSC results.

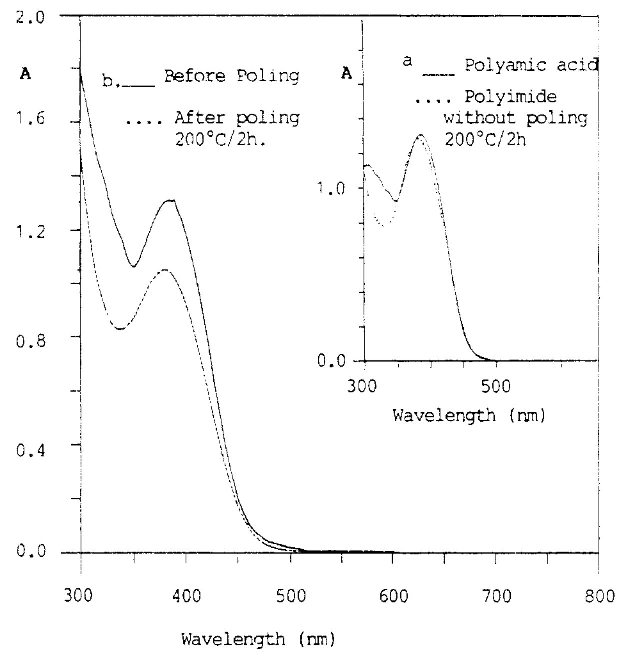


Figure 3. UV/vis spectra of the poly(amic acid) and polyimide: (a) without poling; (b) with poling.

The UV/vis spectrum of the poly(amic acid) showed an absorption maximum at 383 nm due to the (dialkylamino)sulfonylstilbene chromophore. After thermal curing, the absorbance did not change appreciably except for a slight blue shift caused by the matrix change due to imidization. However, after the poly(amic acid) was corona-poled as it was imidized, a large decrease in absorbance was observed due to the birefringence induced by the dipole alignment (Figure 3).

The poly(amic acid) showed an endothermic process at ca. 225 °C as shown by the DSC studies (Figure 4). This process was clearly due to imidization as correlated with the FTIR and UV/vis spectroscopic studies. An exothermic process is also found in the DSC studies at ca. 380 °C, which is certainly due to decomposition of the polymer. TGA studies of poly(amic acid) indicated two weight-loss processes. The one starting at ca. 150 °C due to imidization was absent in the TGA trace of the polyimide. The other starting at ca. 350 °C due to decomposition was present in polyimide. A glass transition was noticed in polyimide at ca. 240 °C. It should be pointed out that this high glass transition temperature does not mean we have to pole the NLO chromophore at the temperature close to 240 °C. Instead, our experiments indicated that the electric poling

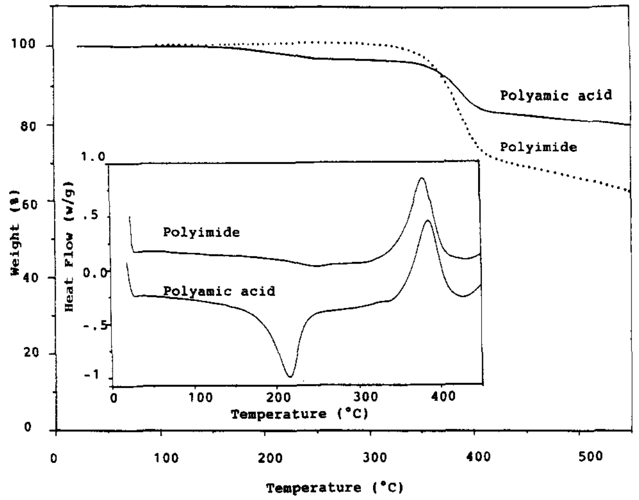


Figure 4. TGA and DSC traces of poly(amic acid) and polyimide.

was effected at ca. 200 °C. A reasonable large order parameter (0.20) was observed after electric poling. This implied that the T_g value of the poly(amic acid) was much lower than that of polyimide; it probably overlapped with the endothermic peak. It is worth mentioning that the poling electric field should be applied before the poly(amic acid) is imidized. Otherwise, the dipole is very difficult to be poled in the rigid polyimide matrix.

Indices of refraction are important optical parameters for the polymers. Elliposometer measurements (using a Rudolph 43603-200E ellipsometer) gave the following Sellmyer's equation: $n(\lambda) = 1.603 + 24300/(\lambda^2 - \lambda_0{}^2)$, where λ_0 is the absorption maximum wavelength of the polyimide at the visible region (383 nm). The accuracy of the measurements is ca. ±0.005.

Second harmonic generation measurements were performed at a wavelength of 1,064 nm. A sizable d_{33} value, 51 pm/V, was obtained. Although the NLO chromophore has an absorption only at 383 nm, this d_{33} value still contains resonant contributions. It is known that, for device applications, a large nonresonant value is of importance. We estimated the nonresonant value of this material by using an approximate two-level model. It was found that the disperseless d_{33} value of the polyimide was ca. 18 pm/V.

To evaluate the high-temperature stability of our polymers, we studied the temporal stability of the SHG signal. It was found that the SHG signal exhibited no decay at room temperature nor at 90 °C (Figure 5). The decay was noticeable at the initial stage when the sample was kept at 150 °C, and the signal was then stabilized at ca. 85% of its initial value. Reasonably high stability was observed at 170 °C; after 150 h, initial nonlinearity of almost 60% was retained (see the inset in Figure 5). This inset shows two sets of data obtained from two samples poled at the same conditions, indicating the reproducibility of the measurements. Several very promising features of this polyimide system can be seen from these results. Its nonlinearity can be stabilized at 90 °C for a long time, which is the possible working temperature anticipated by device engineers. The film can withstand high processing temperatures for a short term (e.g., 200 °C). Furthermore, this reaction approach can be adopted in synthesizing different materials. We can obviously vary several structural parameters to obtain new materials. For example, the NLO chromophore can be changed from the stilbene to other structures which will lead to an improved NLO activity and higher thermal stability. Different dianhydride monomers can be utilized to synthesized polyimide so that the high temperature stability can be further enhanced. Due to the good processability of the poly(amic acid), it is possible to fabricate several device elements.

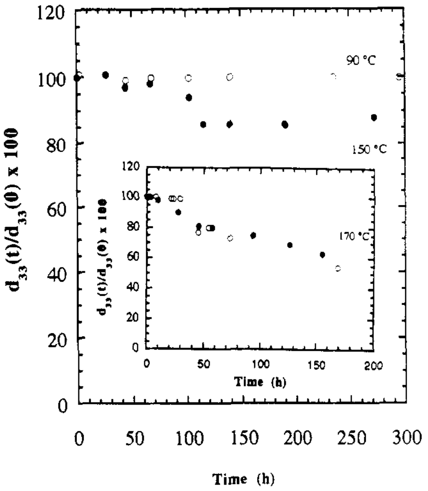


Figure 5. Temporal stability of the SHG signals at various temperatures. The inset shows two sets of data (dotted and circled) obtained from two samples which are poled at the same conditions.

Conclusion

Functionalized aromatic polyimide with pendent nonlinear optical chromophores can be synthesized by careful design of a suitable NLO chromophore. The poly(amic acid) obtained is soluble in several aprotic polar solvents, permitting thin film processing. The polyimide exhibited a high glass transition temperature (240 °C) after the poly(amic acid) was imidized at ca. 200 °C. The high glass transition temperature of the polyimide resulted in a high stability of the optical nonlinearity at elevated temperatures. Long-term stability was observed at 170 °C.

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