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Functionalized Polyimides Exhibiting Large and Stable Second-Order Optical Nonlinearity

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ABSTRACT: A new family of functionalized second-order nonlinear optical polyimides has been developed. The key step in synthesizing these polymers was the syntheses of diamino NLO chromophores, which was accomplished by utilizing the Mitsunobu reaction. The polyimides were obtained from the corresponding poly(amic acids) which exhibited good solubility in aprotic polar solvents, permitting device processing. High glass transition temperatures were obtained in these polyimides, rendering a high stability in dipole orientation at elevated temperatures. The second harmonic generation signals exhibited no decay at room temperature or at 90 °C. A long term stability at 170–180 °C was observed.

Introduction

In the past decade, the research on nonlinear optical polymers has made significant progress in both the fundamental understanding of the mechanism and the design of novel polymer systems.[1-3] Several important issues were identified and need to be studied thoroughly in order to utilize these materials in practical devices. Some of these issues are the long term stability of the nonlinear optical (NLO) activity, larger NLO coefficient, and minimum optical loss. However, the crucial issue is the long term stability of the dipole orientation induced by an electric field. Recently, we synthesized a nonlinear optical polyimide with a very large and exceptionally stable second harmonic generation (SHG) coefficient.[4] The rationale to synthesize this polymer was that the motion of the free volume in the polymer matrix can be frozen due to a high glass transition temperature. The induced dipole orientation could be stabilized in a certain temperature range. Previous works by Wu et al.,[5] Marks et al.,[6] and Dalton et al.[7] demonstrated the promising properties of polyimide systems. Our work represents significant progress in the design, synthesis, and physical properties of second-order NLO polyimides. This paper further elaborates the synthetic versatility of our approach and reports detailed results on the synthesis and physical characterizations.

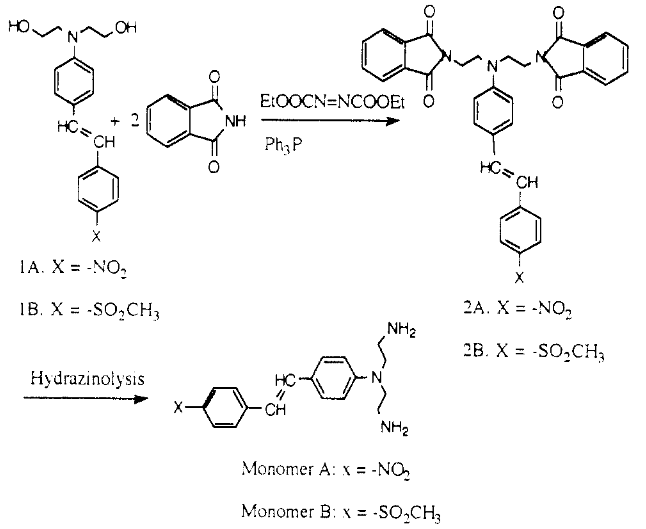
Experimental Section

THF was purified by distillation over sodium chips and benzophenone. DMAc and NMP were purified by distillation over phosphorus pentoxide. Pyromellitic dianhydride (monomer C) was purified by recrystallization from acetic anhydride and dried under a vaccum at 150 °C overnight before use. All of the other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.

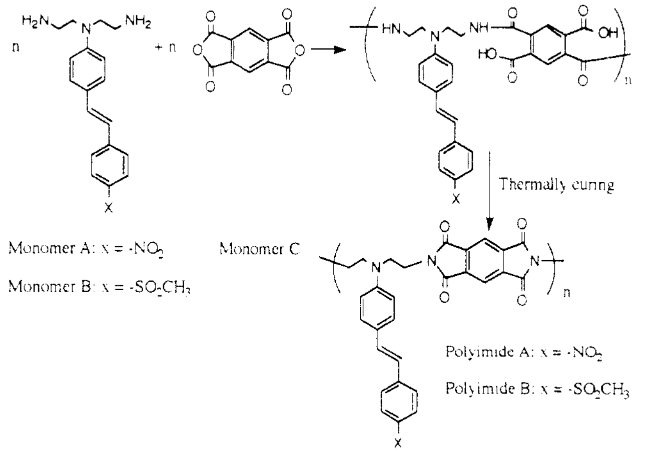
Syntheses of Monomers and Polymers. The synthetic approaches for monomers and polymers are outlined in Schemes 1 and 2 where compounds **1A** and **1B** were synthesized according to the method described in our previous work.[8]

Compound 2A. Diethyl azodicarboxylate (DEAD) (2.389 g, 13.7 mmol) in THF (6 mL) was added dropwise into a solution of compound **1A** (1.5 g, 4.57 mmol), triphenylphosphine (3.598 g, 13.7 mmol), and phthalimide (2.018 g, 13.7 mmol) in THF (20 mL). The resulting mixture was stirred overnight, and the product precipitated out. The red solid was collected by filtration and recrystallized from chloroform/hexane to yield compound **2A** (1.52 g, 56.7%, mp 227–228 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 3.68 (t, J = 7.03 Hz, 4 H, —NCH_2—), 3.89 (t, J = 6.9 Hz, 4 H, —CH_2O—), 6.79 (d, J = 16.2 Hz, 1 H, vinyl proton), 6.89 (d, J = 8.4 Hz, 2 H, aromatic protons), 7.04 (d, J = 16.2 Hz, 1 H, vinyl proton), 7.30 (d, J = 8.4 Hz, 2 H, aromatic protons), 7.49 (d, J = 8.5 Hz, 2 H, aromatic protons), 7.65 (m, 4 H, phathalimide protons), 7.78 (m, 4 H, phathalimide protons), 8.13 (d, J = 8.4 Hz, 2 H, aromatic protons). Anal. Calcd for $C_{34}H_{26}N_4O_6$: C, 69.6; H, 4.4; N, 9.6. Found: C, 69.37; H, 4.52; N, 9.50.

Scheme 1. Syntheses of Diamino NLO Chromophores



Scheme 2. Syntheses of Poly(amic acids) and Polyimides



Compound 2B. This compound was synthesized in a procedure similar to that for compound **1A**. The yellow solid obtained was recrystallized twice from methylene chloride to

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give compound **2B** (4.8 g, 69.2%, mp 215-216 °C). ^{1}H NMR (DMSO-d_6): δ 3.19 (s, 3 H, $-SO_2-CH_3$), 3.60 (t, J = 5.81 Hz, 4 H, $-NCH_2-$), 3.73 (t, J = 6.07 Hz, 4 H, $-CH_2O-$), 6.82 (d, J = 8.05 Hz, 2 H, aromatic protons), 6.99 (d, J = 16.24 Hz, 1 H, vinyl proton), 7.22 (d, J = 16.46 Hz, 1 H, vinyl proton), 7.36 (d, J = 4.07 Hz, 2 H, aromatic protons), 7.69 (d, J = 8.01 Hz, 2 H, aromatic protons), 7.8 (m, 10 H, 8 H for phathimide protons and 2 H for aromatic protons). Anal. Calcd for $C_{35}H_{29}N_3O_6S$: C, 67.84; H, 4.72; N, 6.78. Found: C, 67.67; H, 4.82; N, 6.68.

Monomer A. To a two-neck flask containing compound 2A (0.800 g, 1.36 mmol) and THF (20 mL) was added the hydrazine hydrate (0.389 g, 6.80 mmol). The mixture was refluxed for 5 h under nitrogen and then cooled to room temperature. The precipitate was filtered out, and the filtrate was dried under a vacuum to yield a red solid. Ethanol (20 mL) was then added to this solid and the resulting mixture was stirred for 15 min at ca. 50 °C. The insoluble part was removed by filtration. Deoxygenated water was then added dropwise to the filtrate, and the dark red product crystallized out. The crude product was recrystallized from MeOH/water to yield monomer A (dark-red plate crystals, 0.2 g, 46.2%, mp 160.2 °C (DSC result)). ^{1}H NMR (DMSO-d_6, ppm): δ 1.50 (d, J = 4.07 Hz, 4 H, amine protons), 2.67 (t, J = 6.90 Hz, 4 H, $-CH_2NH_2$), 3.31 (t, J = 6.98 Hz, 4 H, $-CH_2N-$), 6.71 (d, J = 8.37 Hz, 2 H, aromatic protons), 7.03 (d, J = 16.31 Hz, 1 H, vinyl proton), 7.36 (d, J = 16.32 Hz, 1 H, vinyl proton), 7.41 (d, J = 8.33 Hz, 2 H, aromatic protons), 7.702 (d, J = 8.36 Hz, 2 H, aromatic protons), 8.12 (d, J = 8.40 Hz, 2 H, aromatic protons). Anal. Calcd for $C_{18}H_{22}N_4O_2$: C, 66.23; H, 6.80; N, 17.17. Found: C, 66.04; H, 6.75; N, 17.06.

Monomer B. The hydrazine hydrate (3.0 g, 60 mmol) in THF (10 mL) was added slowly to a suspension of compound **2B** (3.05 g, 5.0 mmol) in 40 mL of THF under stirring. The mixture was refluxed for 3 h under nitrogen and then cooled to room temperature. The solid was removed by filtration, and the filtrate was concentrated under vacuum to ca. 5 mL. Ethanol (10 mL) was added to the concentrated filtrate, and the solution was placed in a refrigerator overnight. The yellow crystals were collected and recrystallized twice from ethanol, yielding monomer B (0.77 g, 42.8%, mp 105-106 °C). ^{1}H NMR (DMSO-d_6): δ 2.66 (t, J = 6.55 Hz, 4 H, H_2NCH_2-), 3.18 (s, 3 H, $-SO_2CH_3$), 3.31 (t, J = 6.64 Hz, 4 H, $-NCH_2-$), 6.70, 7.38, 7.70, 7.79 (d, 2 H, aromatic protons), 7.00, 7.27 (d, 1 H, vinyl protons). Anal. Calcd for $C_{19}H_{25}N_3O_2S$: C, 63.49; H, 7.01; N, 11.69. Found: C, 63.54; H, 6.97; N, 11.49.

Poly(amic acid) A. To a 25-mL two-neck round bottom flask were added monomer A (0.1610 g, 0.74 mmol) and NMP (2 mL). The solution was stirred for 15 min at 0 °C and the pyromellitic dianhydride (0.2407 g, 0.74 mmol) was then added at once with vigorous stirring at 0 °C. The mixture was stirred at 0 °C for 3 h and at room temperature for another 12 h. The resulting polymer solution was used to prepare films directly without separation. To further characterize the polymers, the poly(amic acid) was precipitated into methanol and the polymer was collected by filtration. After washing with acetone overnight in a Soxhlet extractor, the polymer was collected as a dark red solid. The ^{1}H NMR spectrum of poly(amic acid) A is presented in Figure 1.

Poly(amic acid) B. To monomer B (0.359 g, 1.0 mmol) in DMAc (4.0 mL) was added the pyromellitic dianhydride (0.218 g, 1.0 mmol) at once at 20 °C under nitrogen. The resulting mixture was stirred at 20 °C overnight. The polymer solution was handled in the same way as poly(amic acid) A, and a yellow solid was obtained. The ^{1}H NMR spectrum of the poly(amic acid) is shown in Figure 1.

Polyimide. The poly(amic acid) films were dried at 50 °C and then heated sequentially at 100 °C for 1 h, 180 °C for 2 h, and 200 °C for 5 h. The imidization process was monitored by FTIR, UV/vis, DSC, and TGA measurements.

Characterization. The ^{1}H NMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. The FTIR spectra were recorded on a Nicolet 20SXB 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 without corrections. Elemental analyses were performed by Atlantic Microlab, Inc.

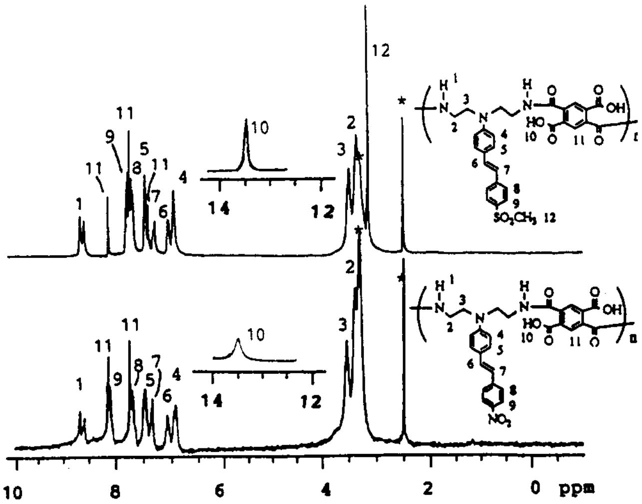

Figure 1. ^{1}H NMR spectra of poly(amic acids) A and B in DMSO-d_6.

To prepare films for second harmonic measurements, a poly(amic acid) solution in DMAc (or NMP) was filtered through a 0.2-μm syringe filter 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 dried under a vacuum at 60 °C overnight. To further align the dipole moment of the NLO chromophore, the films were electrically poled and thermally cured simultaneously in a corona-discharge setup. The discharging needle-to-plane distance was 1.0 cm, and the temperature was gradually increased as follows: 60-120 °C, 30 min; 120-150 °C, 30 min; 150-200 °C, 30 min; 200-220 °C, 1 h. The sample was cooled to room temperature in the presence of the poling electric field (field strength, 2.5 MV/cm).[9] The refractive indices of the polyimides were measured by using a Rudolph 43603-200E ellipsometer at several wavelengths. The results were utilized in fitting the Sellmeyer equation to obtain refractive indices at the desired wavelengths.

The second harmonic generation (SHG) of the poled polymeric films was measured by using a model-locked Nd:YAG laser (Continuum-PY61C-10 with a pulse width of 25 ps and a repetition rate of 10 Hz) as a fundamental light source (1.064 μm). A photomultiplier tube (PMT) was used to detect the second harmonic signal which was amplified and averaged in a boxcar integrator. The temporal stability of the SHG signals of the polyimides were monitored at various temperatures. The error of the temperature reading in the vacuum oven used was within ±5 °C.

Results and Discussion

Syntheses of monomers and polymers. The Mitsunobu reaction with modified conditions has been applied to synthesize monomers A and B, as shown in Scheme 1.[4,10] It was found that the Mitsunobu reaction transformed the hydroxyl groups smoothly into phthalimides in a reasonable yield. Due to the poor solubility of compound 2 in ethanol, we chose THF as the solvent in the next hydrazinolysis step. It was found that after hydrazinolyzing the phthalimide, the diamino monomers could be separated simply by filtration and recrystallization. Treatment with hydrochloric acid was not necessary.[4,10] Elemental analysis showed that pure monomers were obtained.

The polycondensation reaction between the aromatic dianhydrides and the diamino monomers were carried out in NMP, DMF, or DMAc at room temperature. Reasonable molecular weights were obtained. The intrinsic viscosity measurements indicated values of 0.4 and 0.28 dL/g for poly(amic acids) A and B, respectively.

Structural Characterizations. Various spectroscopic techniques were used to study the structures of the poly(amic acids). The ^{1}H NMR spectra of poly(amic acids) A and B are shown in Figure 1. In both poly(amic acids), the chemical shift of the methylene units linked with the primary amines was changed from 2.7 to 3.4 ppm after the formation of the amide. The chemical shift of the other methylene units linked with the tertiary amine were changed only from 3.3 to 3.6 ppm. The chemical shifts due to the stilbene units were identical with those in corresponding monomers except the chemical shift due to proton 4 in poly(amic acid) A which shifted slightly (from 6.7 to 6.9 ppm, see the numbering of protons in Figure 1). The chemical shift due to the methylsulfonyl group in poly(amic acid) B appeared at 3.15 ppm. Two peaks at 8.55 and 8.70 ppm were evident due to amide protons. The chemical shifts due to the carboxylic acid protons appear at ca. 13.5 ppm. Three sharp peaks can be noted in the spectrum of poly(amic acid) B, which were ascribed to proton 11 at trans (7.75 ppm) and cis (7.4 and 8.2 ppm) amide linkages. Two similarly sharp peaks can be seen in the spectrum of poly(amic acid) A, another peak overlapped with the peak due to proton 5.

The FTIR spectra of both poly(amic acids) showed clearly the bands due to the carbonyl groups in amide linkages at 1719 cm^{-1} and in carboxylic acid at 1651 cm^{-1} (Figure 2). Two strong absorption bands due to the nitro group in the NLO chromophore of poly(amic acid) A appeared at 1337 and 1516 cm^{-1}, respectively. These results were consistent with the structure as proposed.

After thermal curing, The FTIR spectrum showed a dramatic change. New bands at 1772 (carbonyl asymmetric stretching), 1382, 1150, and 726 cm^{-1} appeared. These are typical changes accompanying the imidization process.[11] The band at 1650 cm^{-1} completely dissappeared after the polymer film was cured at 200 °C overnight. However, the bands due to the nitro group on the NLO chromophore of polymer A did not change appreciably in intensity, indicating that the NLO chromophore survived during the curing process.

The UV/vis spectra of both the poly(amic acids) and the polyimides exhibited a typical absorption pattern due to the stilbene type NLO chromophores (see Figure 3 and ref 4). Poly(amic acids) A and B exhibited absorption maxima at ca. 450 nm and 381 nm, respectively. The samples without poling showed a blue shift, and their absorbances remained the same before and after imidization at ca. 200 °C as shown in Figure 4 for polymer B. However, after electric poling, the dipole moments of the NLO chromophores were aligned and the UV/vis spectra of polyimides exhibited a blue shift and a decrease in absorption due to birefringence. From the absorbance change, the order parameters of the poled films can be estimated. Under the conditions of a 5-kV poling field at 200 °C, the order parameter values of 0.30 and 0.12 were deduced for polyimides A and B, respectively.

Thermal Properties. Polyimide A was thermally stable up to 340 °C under a nitrogen atmosphere, while poly(amic acid) A started to lose weight at about 150 °C due to imidization, as shown by the TGA studies (Table 1). Polyimide A exhibited two decomposition processes which could be attributed to the decomposition of the NLO chromophore (340 °C) and that of polyimide backbone (420 °C). The detailed decomposing mechanism is unclear. Polyimide B seemed to be more stable than polyimide A. The TGA trace of polyimide B showed that thermal decomposition started at 437 °C under a nitrogen atmosphere. The corresponding poly(amic acid) B started imidization at ca. 180 °C. The imidization process was completed as the temperature reached 250 °C, as shown in both the TGA and DSC traces (insets in Figure 4). This indicated that to imidize the sample, the curing temperature can be set at about 200 °C (the peak of the endothermic process) under nitrogen without the risk of damaging the materials. After imidization, the polyimides exhibited glass transition temperatures of 230 and 250 °C (See Table 1).

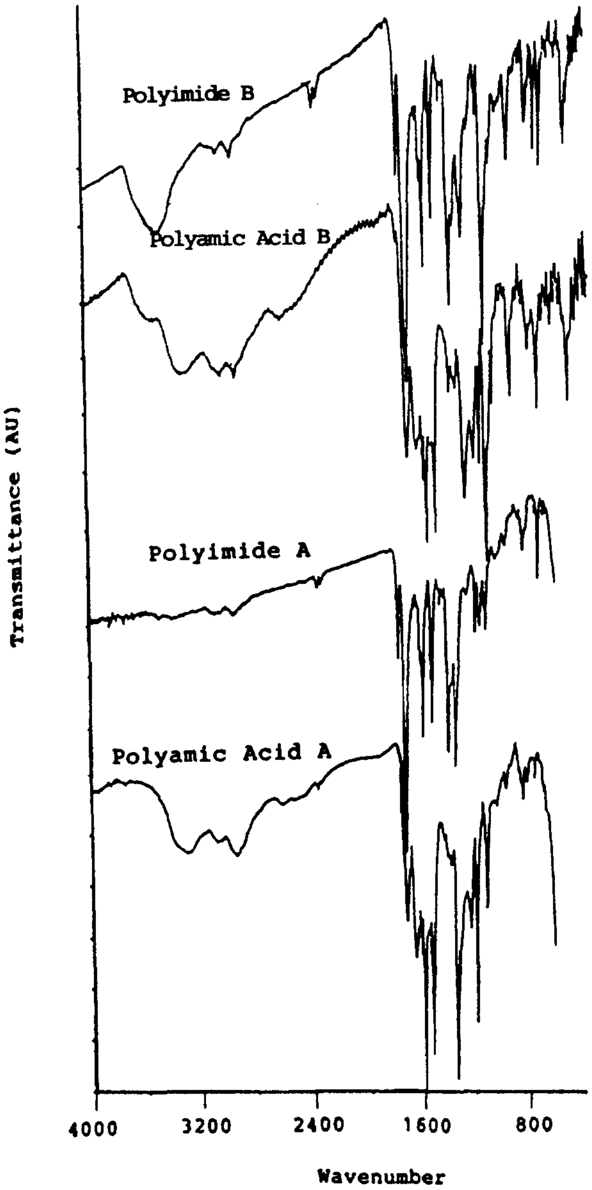

Figure 2. FTIR spectra of poly(amic acids) A and B and polyimides A and B.

Physical Characterization. Table 2 listed the results of several physical measurements of the polyimides. Second harmonic generation measurements, performed at a wavelength of 1064 nm, revealed a very large d_{33} value, 115 pm/V, for polyimide A. For polyimide B, a d_{33} value of 28.8 pm/V was observed. It was clear that polyimide A exhibited a much larger optical nonlinearity as anticipated from the β values of the corresponding NLO chromophore. Since the second harmonic wavelength was at 532 nm, which is in the absorptive region of polyimide A, there was a large resonant contribution to this d_{33} value. Although polyimide B has a maximum absorption at 381 nm, a certain amount of resonant enhancement existed in the observed value at 532 nm. Since we do not have a longer wavelength laser source, we evaluated the non-

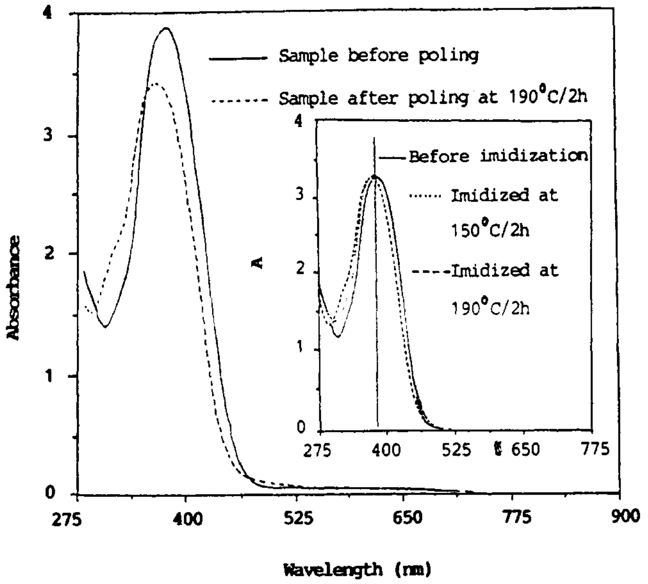

Figure 3. UV/vis spectra of poly(amic acid) B and polyimide B (with and without electric poling).

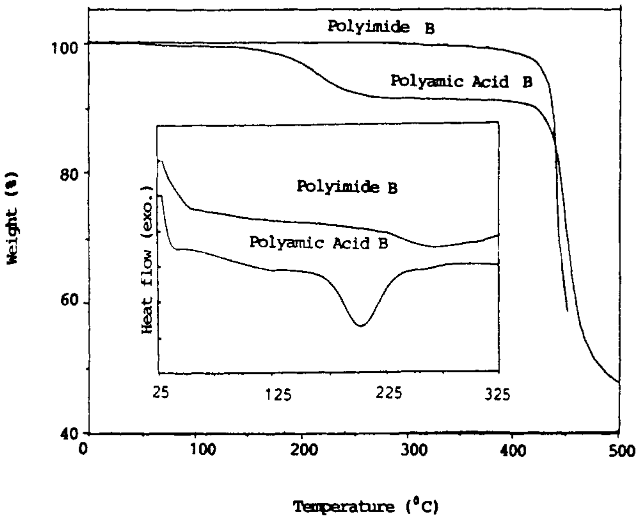

Figure 4. TGA and DSC (insets) traces of poly(amic acid) B and polyimide B.

Table 1. Physical Properties of the Polymers

polymers	[η], dL/g	T_{decom},^{a} °C (TGA)	thermal processes in DSC, °C	λ_{max}, nm
poly(amic acid) A	0.40	182, 340	176^b (endo, ΔH_{max})	445
poly(amic acid) B	0.28	185, 240, 436	200^b (endo, ΔH_{max})	381
polyimide A		340, 420	230 (T_g)	440
polyimide B		437	250 (T_g)	372

^{a} Onset temperature (the temperature at the intersection of the first and second tangents). ^{b} Peak temperature.

Table 2. Optical Properties of the Polyimides

polyimide	λ_{max}, nm	order parameter	n (532 nm)	n (1064 nm)	d_{33} (532 nm), pm/V	d_{33} (∞), pm/V
A	440	0.30	1.833	1.746	115	27
B	372	0.12	1.769	1.625	28.8	10

resonant value of these materials by using an approximate two-level model.[12] It was found that the disperseless d_{33} value of polyimide A was ca. 27 pm/V and ca. 10 pm/V for polyimide B (see Table 2).

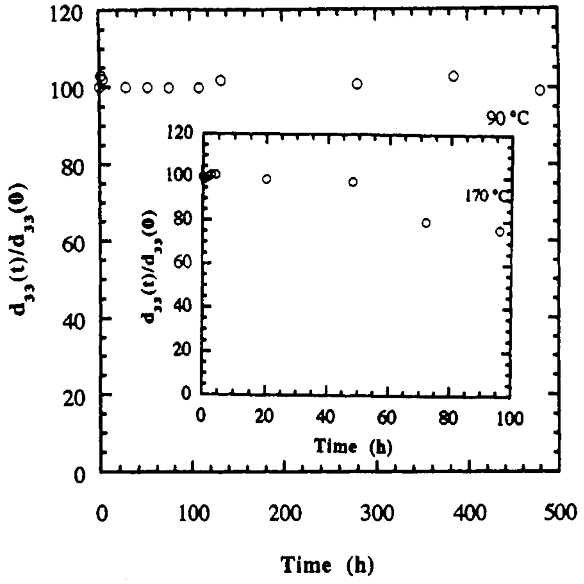

Figure 5. Temporal stability of the second harmonic generation signal of polyimide B at various temperatures.

The motivation to synthesize these polyimide materials was the expectation that they may exhibit a high stability at elevated temperatures. It is a very important requirement for their practical applications in electro-optic devices. To evaluate the high temperature stability of these polymers, we studied the temporal stability of second harmonic generation (SHG) signals at various temperatures. For polyimide A, it was found that the SHG signal exhibited no decay at room temperature or at 90 °C. When the SHG signal of the polymer films was monitored at 150 °C, an initial decay of 15% was observed and the signal was then stabilized at that level. We further studied the stability at 180 °C, the decay was sped up due to a faster relaxation of the dipole orientation. However, the SHG signal was clearly stable enough to withstand such a high temperature environment for a reasonably long term; after almost 1.5 h, ca. 70% of the SHG signal was retained.[4] A similar behavior was observed for polyimide B (Figure 5). No decay in SHG signal was observed at 90 °C. Long term stability at 170 °C was observed. These results indicated that these materials are very promising for practical applications: their nonlinearities could be stabilized at 90 °C for a long time. The film could withstand a short term of high processing temperature. Due to the good processibility of the poly(amic acids), many device elements are possible to be fabricated.

Conclusion

We synthesized a new family of functionalized NLO polyimides which exhibited exceptional stabilities at elevated temperatures. The key step was the synthesis of a diamino NLO chromophore which was accomplished by utilizing the Mitsunobu reaction. Due to the versatility of the reaction scheme, many new materials can be expected.

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