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Highly Stable Copolyimides for Second-Order Nonlinear Optics

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ABSTRACT: Nonlinear optical (NLO) copolyimides exhibiting high glass transition temperatures (T_g) and high thermal stabilities were synthesized to achieve long-term stability of optical nonlinearity at elevated temperatures. The relationship between the chromophore loading level and the physical properties of the copolymers was studied. It was found that decreasing the chromophore loading level increased the glass transition temperature more than 40 °C. As a result, the stability of the electric field induced dipole orientation of the nonlinear optical chromophores was enhanced. The second harmonic generation (SHG) signal maintained 85% of its initial value after 700 h at 180 °C. Sizable second-order nonlinear optical coefficients and electro-optic coefficients were obtained.

Introduction

Polyimides, especially aromatic polyimides, are of growing interest in the investigation of second-order nonlinear optical (NLO) materials because of their high glass transition temperatures which can be utilized to stabilize the dipole orientation of the NLO chromophore at high temperatures.[1−5] Another attractive feature of polyimides is their high thermal stability that enables them to survive at elevated temperatures during fabrication and operation in integrated optoelectric devices. In previous work, we described a general approach to synthesize a series of aromatic polyimides functionalized with pendant NLO chromophores.[2,3] Their structure−property relationship has been systematically studied. We observed that polyimides with the same NLO chromophore but different dianhydrides have distinct physical properties, such as thermal stability and optical nonlinearity. It was also found that these functionalized polyimides exhibit glass transition temperatures that are consistently lower than those of the corresponding nonfunctionalized polyimides. It can be expected that if the common diamino monomers, for example, 1,4-phenylenediamine, are used in conjunction with diamino monomers bearing NLO chromophores and corresponding dianhydrides, NLO copolyimides can be synthesized. This copolymerization approach will offer the opportunity to study the effects of the chromophore loading level on the glass transition temperaure (T_g), the thermal stability, and the optical nonlinearity (the chromophore loading level is defined as the weight percentage of the chromophore unit in the polymer). Thorough understanding of these relationships is important to further enhance the performance of the NLO materials. The copolyimides exhibited higher glass transition temperatures and better thermal performances of the NLO properties than previous polyimides. However, the NLO properties diminished due to the reduced NLO chromophore loading level. The results indicate that the copolyimides are the materials of choice for high thermal stability within a tolerable trade-off range in optical nonlinearity. In this paper, we discuss the detailed experimental results.

Experimental Section

A diamino monomer with a chromophore of Disperse Red 1 was synthesized by an approach described previously.[2,3,6] The 1,4-phenylenediamine was purifed by recrystallization from methanol. All other chemicals were purchased from Aldrich Chemical Co. and used as received.

Polymerization. The synthesis of polyimide **PI 1** was described in a previous paper.[3] The following polymerization procedure exemplifies the synthesis of copolyimides **PI 2**−**6**. To a mixture of diamino monomer (0.1825 g, 0.434 mmol) and 1,4-phenylenediamine (0.0156 g, 0.145 mmol) in 5 mL of NMP at 0 °C was added 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (0.2571 g, 0.579 mmol) under nitrogen. After stirring for 1 h at 0 °C and then at room temperature for an additional hour, the resulting poly(amic acid) was imidized using a mixture of acetic anhydride and pyridine (10 mL/5 mL, 2:1). The mixture was stirred at room temperature for 2 h and then heated to 90 °C for another 3 h. The polymer was precipitated into methanol (100 mL) and collected by suction filtration. The solid was further purified by repeated dissolution in NMP and precipitation into methanol. The collected polymer was washed with methanol in a Soxhlet extractor for 2 days and then dried under a vacuum at 60 °C for 2 days. The ^{1}H NMR spectra of **PI 2**−**6** are similar except for the relative magnitude of the peaks.

PI 1: 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.

PI 2: Anal. Calcd for $C_{37}H_{22}F_6N_5O_{6.25}$: C, 59.20; H, 2.93; N, 9.33. Found: C, 58.98; H, 3.02; N, 9.40.

PI 3: Anal. Calcd for $C_{33}H_{18}F_6N_4O_{5.5}$: C, 58.93; H, 2.68; N, 8.33. Found: C, 58.92; H, 2.73; N, 8.30.

PI 4: Anal. Calcd for $C_{30.33}H_{15.33}F_6N_{3.33}O_5$: C, 58.70; H, 2.47; N, 7.53. Found: C, 58.53; H, 2.70, N, 7.48.

PI 5: Anal. Calcd for $C_{29}H_{14}F_6N_3O_{4.75}$: C, 58.59; H, 2.36; N, 7.07. Found: C, 58.36; H, 2.53; N. 7.00.

PI 6: Anal. Calcd for $C_{28.2}H_{13.2}F_6N_{2.8}O_{4.6}$: C, 58.51; H, 2.28; N, 6.78. Found: C, 57.94; H, 2.54; N. 6.70.

The ^{1}H NMR spectra were collected on a Varian 500-MHz 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 using DSC-10 and TGA-50 systems from TA Instruments. Elemental analyses were performed by Atlantic Microlab, Inc. A Metricon Model 2010 prism coupler was used to measure the refractive indices of the polyimides. A He−Ne laser (632.8 nm) and two diode lasers (780 and 1300 nm) were used as the light sources. The refractive indices of both TE and TM modes were measured at these wavelengths. The Sellmeier equation ($n^2 - 1 = A/(\lambda_0^{-2} - \lambda^{-2}) + B$) was employed to deduce the refractive indices at the laser wavelengths of interests such as 1064 and 532 nm, where λ_0 is the absorption maximum wavelength, λ is the wavelength at which the refractive index is to be determined, A is a constant proportional to the chromophore oscillator strength, and B accounts for all other absorption contributions.[7]

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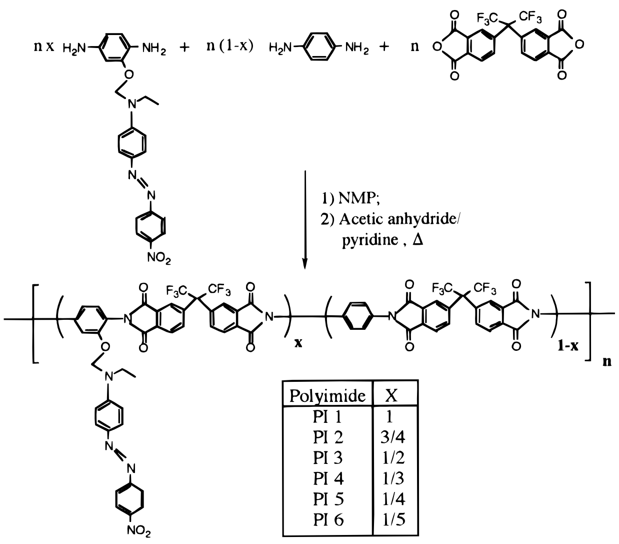
Scheme 1. Synthesis of Aromatic Copolyimides



Polyimide	X
PI 1	1
PI 2	3/4
PI 3	1/2
PI 4	1/3
PI 5	1/4
PI 6	1/5

Table 1. Molecular Weights of the Copolyimides

	PI 1	PI 2	PI 3	PI 4	PI 5	PI 6
x	1	3/4	1/2	1/3	1/4	1/5
M_n	14000	16000	15000	12000	10000	9000
M_w	35000	38000	43000	49000	33000	28000
polydispersity	2.5	2.4	2.9	4.2	3.3	3.3

The polyimide films were prepared by casting or spin-coating the polymer solution in tetrachloroethane (TCE) onto a glass slide or an indium tin oxide (ITO) glass slide. The thickness of the spin-coated film was around 0.5–2 μm depending upon the concentration and viscosity of the polymer solution. The films were then coated with a thin layer of polystyrene. The copolyimides were poled using the corona discharge method. The distance from the needle electrode to the surface of the polymer film was fixed at 1 cm, and the applied electric field was set as high as 6000 V. After poling, the polystyrene buffer layer was removed using benzene.

The polyimide films were characterized by a second harmonic generation experiment using a mode-locked Nd:YAG laser (Continuum PY61C-10, 10-Hz repetition rate) 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 crytal was used as the reference sample. The temperature-dependent second harmonic generation was conducted with the same apparatus.

Films for the measurements of the electro-optic coefficient were prepared by corona poling, on which a silver electrode of 1000 Å was then deposited by vacuum evaporation. The electro-optic coefficients (r_{33}) were determined by the simple reflection technique at 1300 nm.[8]

Results and Discussion

The copolyimides were synthesized via poly(amic acid)s followed by chemical imidization (Scheme 1). They are soluble in solvents such as THF, chloroform, NMP, tetrachloroethane, DMF, and DMSO. The polymer with a relatively low chromophore loading level possesses relatively poor solubility in THF and chloroform.

These polyimides exhibit number-average and weight-average molecular weights in the range $\bar{M}_n = 9000$–16000 Da and $\bar{M}_w = 28000$–49000 Da (Table 1). The elemental analyses gave an excellent match with the theoretical values.

The ^{1}H NMR spectra of copolyimides **PI 2–6** all show one peak at 7.6 ppm due to the four aromatic protons in the phenyl group without NLO chromophores. When the ratio of the 1,4-phenylenediamine over the NLO diamine increased, the integration of the peak at 7.6 ppm gradually increased. The compositions of the copolyimides were well correlated in comparison to the integration of the peaks in the aliphatic region which were solely due to the NLO chromophore.

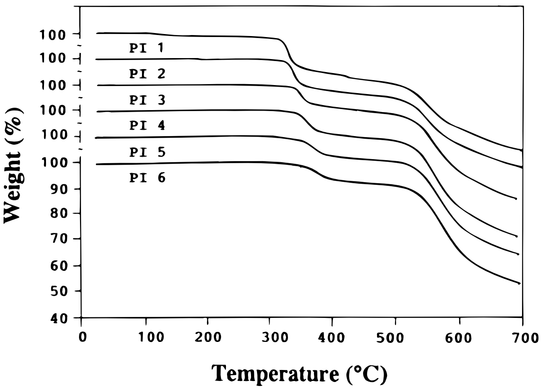


Figure 1. TGA traces of copolyimides with a heating rate of 10 °C/min under a nitrogen atmosphere.

Table 2. Physical Properties of PI 1–PI 6

	PI 1	PI 2	PI 3	PI 4	PI 5	PI 6
x	1	3/4	1/2	1/3	1/4	1/5
chromophore loading level (%)	32.3	26.8	19.9	14.4	11.3	9.3
T_g (°C)	235	236	257	267	277	278
T_d (°C)	319	327	342	344	348	354
λ_{max} (nm)	477	477	477	478	477	476
Φ	0.18	0.19	0.18	0.17	0.21	0.19
d_{33} (532 nm) (pm/V)	146	115	70	51	38	32
$d_{33}(\infty)$	16	14	9	7	5	4
r_{33} (1300 nm) (pm/V)	25	19	11	10	4	3

The FTIR spectra of all the polymers exhibited two characteristic absorption bands at 1785 and 1730 cm^{-1} due to the stretching modes of the imide rings. The absorption peaks of the nitro groups occurred at 1518 and 1340 cm^{-1}. These results support the imide structure and indicate the existence of the NLO chromophore.

Thermal Properties. DSC studies indicated that as the NLO chromophore loading level decreased, the glass transition temperature (T_g) of the copolyimides gradually increased from 235 to 278 °C (Table 2). The high glass transition temperatures of these polymers require a high thermal stability of NLO chromophores because the polymer film has to be poled around its glass transition temperature to induce optical nonlinearity. The TGA studies (Figure 1) showed that the decomposition temperatures (the onset point at which the sample starts the weight loss) of these copolyimides were higher than the corresponding glass transition temperatures (320 vs 235 °C for **PI 1** and 345 vs 278 °C for **PI 6**). This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophores. Isothermal experiments for **PI 6**, by ramping the temperature to 300 °C and maintaining the temperature at 300 °C for 2 h either in the nitrogen or in the air flow, showed only a slight decrease in the TGA trace (Figure 2). It is also interesting to note that the temperature for the occurrence of the first weight loss corresponding to the decomposition of the NLO chromophore gradually increased as the chromophore loading level decreased while all the copolyimides have almost the same second weight loss at 520 °C due to the decomposition of the backbone of the copolyimides.

Linear Optical Properties. When the chromophore loading level decreased, the refractive indices decreased (Table 3). This feature is interesting because it provides the opportunity of fine-tune the linear optical properties

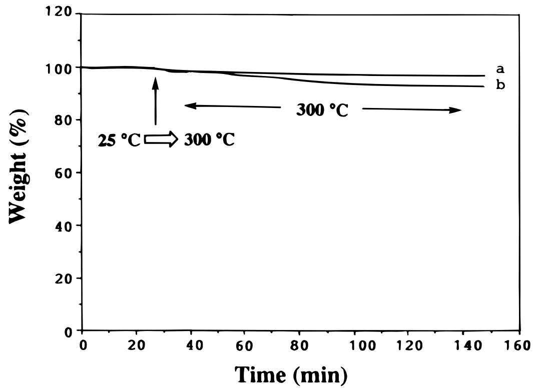


Figure 2. TGA trace of **PI 6** isothermal at 300 °C for 2 h: (a) in the N_2 flow; (b) in the air flow.

Table 3. Refractive Indices of TE and TM Modes at Different Wavelengths

polymer	wavelength (nm)	unpoled sample		poled sample	
		n_{TE}	n_{TM}	n_{TE}	n_{TM}
PI 1	632.8	1.7399	1.7172	1.7421	1.7410
	780	1.6741	1.6489	1.6729	1.6699
	1300	1.6390	1.6159	1.6403	1.6173
PI 2	632.8	1.7297	1.6934	1.7170	1.7113
	780	1.6662	1.6358	1.6586	1.6527
	1300	1.6238	1.6113	1.6226	1.6165
PI 3	632.8	1.6856	1.6555	1.6839	1.6801
	780	1.6494	1.6180	1.6415	1.6374
	1300	1.6178	1.5874	1.6114	1.5910
PI 4	632.8	1.6639	1.6398	1.6669	1.6421
	780	1.6252	1.6010	1.6317	1.6040
	1300	1.5963	1.5730	1.6020	1.5799
PI 5	632.8	1.6428	1.6111	1.6427	1.6224
	780	1.6140	1.5858	1.6154	1.5939
	1300	1.5918	1.5663	1.5911	1.5702
PI 6	632.8	1.6376	1.6196	1.6407	1.6144
	780	1.6112	1.5856	1.6117	1.5890
	1300	1.5899	1.5660	1.5901	1.5661

of the polymers to suit the needs of the device applications. These polymers are birefringent in their pristine films as evidenced by the difference between the refractive indices of the TE and TM modes. The refractive indices of the TE mode (in-plane) are larger than those of the TM mode (out-of-plane), which implies that the polyimide backbone might lie in the plane of the film. The refractive indices of the TE mode did not change after corona electrical poling. The refractive indices of the TM mode became larger after poling and the birefringence became smaller simultaneously. This phenomenon is caused by the alignment of the molecules of the chromophore along the direction of the applied poling field, which is perpendicular to the polymer film plane (out-of-plane).

The absorption peak in the UV−vis spectra after poling decreased and the position of the peak slightly blue-shifted, which are typical phenomena for the poled polyimide sample. An important parameter which characterizes the efficiency of the poling is the order parameter, defined as $\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively. To make the physical data comparable among different samples, the order parameters of the copolyimides were maintained around 0.19.

The UV−vis measurement is also one technique capable of evaluating the thermal and optical nonlinearity stability. Control experiments have been done for two polyimide films of **PI 6** (Figure 3). These two films were spin-coated from the same batch of polymer solution so that they had similar thickness; sample A was poled and sample B was unpoled. The absorption peak decreased for sample A after poling. A minor rise later occurred after 1 h and a minor fall after 1 week when the sample was aged at 180 °C in the air. The minor rise for the poled sample, which corresponds to the relaxation process of the dipole alignment, accounts for the removal of the surface charge after poling. The decrease in the absorption peak indicates that the instability of the nonlinearity at high temperatures primarily comes from the thermal decomposition of the chromophore as opposed to the thermodynamic decay of the polar order. Otherwise, if only the relaxation process of the dipole alignment happens, the absorption peak in the UV−vis spectra should increase rather than decrease. For the unpoled sample, only a successive minor reduction in absorbance was observed after 1 week, which was probably due to the minor thermal damage of the chromophore at such a high temperature.

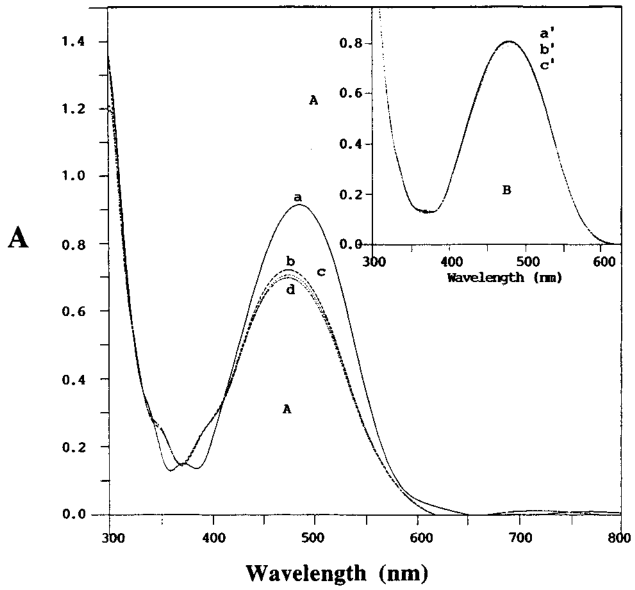


Figure 3. UV−vis spectra of **PI 6** for both poled (A) and unpoled (B) samples: (a) before poling; (b) right after poling; (c) after 1 h of curing at 180 °C; (d) after 1 week of curing at 180 °C; (a′) before curing; (b′) after 1 h of curing at 180 °C; (c′) after 1 week of curing at 180 °C.

Nonlinear Optical Properties. The optical nonlinearity was characterized by two experiments: second harmonic generation (SHG) and electro-optic measurements. All results are listed in Table 2. Second harmonic generation measurements for the poled polyimides were conducted to determine the second harmonic generation coefficients (d_{33}). **PI 1** possessed the highest SHG coefficient at 532 nm ($d_{33} = 146$ pm/V) and its nonresonant value at ∞ nm based upon the approximate two-level model was 16 pm/V.[9] When the chromophore loading level was reduced, both the d_{33} and $d_{33}(\infty)$ values decreased (see Table 2). This relationship is obvious because the d_{33} values are linearly proportional to the concentration of the NLO chromophore.

The electro-optic coefficients (r_{33}) were measured using the simple reflection technique at 1300 nm, which is beyond the absorption band of the chromophore. A large r_{33} value was obtained for **PI 1** ($r_{33} = 25$ pm/V at 1300 nm). A similar trend to d_{33} values exists for r_{33} values in that they become smaller as the chromophore loading level becomes smaller (Table 2).

The temporal stability of SHG was measured at 180 °C. The copolyimides exhibit greatly improved stabilities, compared to the original **PI 1** and other polyimides

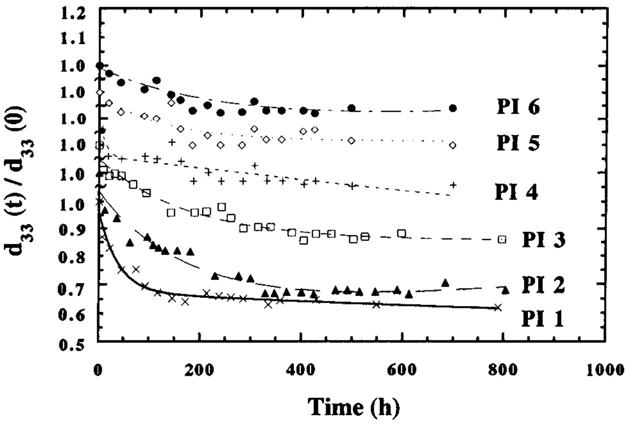


Figure 4. Temporal stability of SHG signals of copolyimides at 180 °C in air.

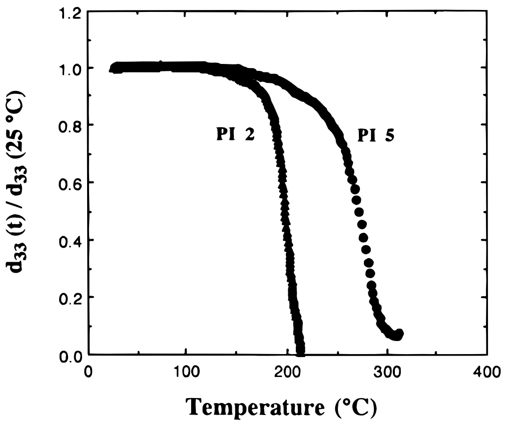


Figure 5. SHG signals of **PI 2** and **PI 5** as a function of temperature.

we synthesized.[3] Few polymers can survive at such high temperatures for a long time. The polymer with a higher T_g possessed a higher stability. Figure 4 shows that **PI 6** with the highest T_g stabilized around 85% of its initial value after 700 h at 180 °C, while **PI 1** with the lowest T_g only exhibited 60% of the original SHG signal after 800 h at the same temperature.

The temperature-dependent SHG was carried out in situ by monitoring the SHG signal while the temperature was ramped in 4 °C/min (Figure 5). **PI 5**, which has a higher T_g shows much better stability than **PI 2** with a lower T_g. Compared with the onset decay temperature (200 °C) for **PI 2**, the onset temperature of 250 °C for **PI 5** is a significant improvement (the onset temperature is the temperature at the intersection of the first and second tangents).

Conclusions

NLO copolyimides with varying NLO chromophore loading levels were synthesized. It was found that as the chromophore loading level decreased, the glass transition temperature increased, as well as the thermal performance of the resulting polymers. Copolymerization provides a general approach to the enhancement of the thermal stability and the nonlinear optical stability of the materials within a tolerable trade-off range in optical nonlinearity.

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Supporting Information Available: NMR data for polyimides **PI 1**–**6**, NMR spectra for polyimides **PI 1**–**6**, and FTIR spectra for polyimides **PI 1**, **3**, and **5** (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Yu, D.; Yu, L. P. *Macromolecules* **1994**, *27*, 6718.
(2) Yu, D.; Gharavi, A.; Yu, L. P. *Macromolecules* **1995**, *28*, 784.
(3) Yu, D.; Gharavi, A.; Yu, L. P. *J. Am. Chem. Soc.* **1995**, *117*, 11680.
(4) Chen, T.; Jen, A. K.-Y.; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295.
(5) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604.
(6) Mitsunobu, O. *Synthesis* **1981**, 1.
(7) Born, M.; Wolf, E. *Principles of Optics*; Pergamon: Oxford, U.K., 1980.
(8) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990**, *56*, 1754.
(9) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

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