Second-Order Nonlinear Optical Polyimide with High-Temperature Stability

Zhonghua Peng and Luping Yu*

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

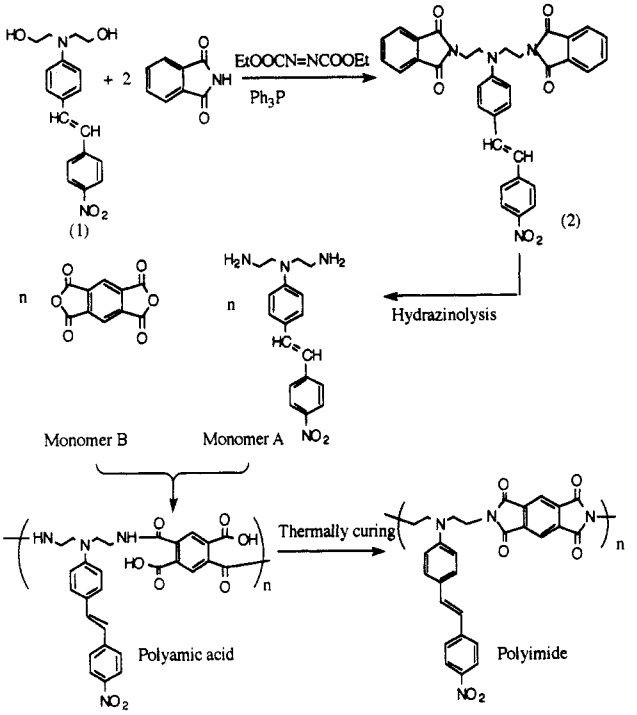
Received December 12, 1993
Revised Manuscript Received February 22, 1994

Although second-order nonlinear optical (NLO) polymers hold promise for practical applications in electrooptical devices, a number of issues have to be thoroughly addressed before they possess commercial value.[1-4] Three of these crucial issues are the high temporal stability of dipole orientation, large optical nonlinearity, and minimum optical loss. Realizing the intrinsic nature of the optical loss (due to C–H overtone vibration absorption), major research efforts have been focused on optimizing the optical nonlinearity and stabilizing the dipole orientation. Different approaches have been taken to address these issues, and considerable progress has been achieved.[1-13] For example, various cross-linking schemes (photochemical and thermal cross-linking) have been developed to lock the dipole orientation in the polymer matrix after electric poling. The temporal stability of second-order NLO activity has been enhanced.[5-13] The rationale in designing these polymers is that, after cross-linking, the motion of the free volume in the polymer matrix can be frozen. This is reflected in the increase of the glass transition temperature of the resulting materials. The same rationale can be transformed into that as long as a polymer has a high glass transition temperature; the induced dipole orientation can be stabilized in a certain temperature range. This was clearly demonstrated in several second-order NLO polyimide composite materials.[14] More recently, Marks et al.[15] and Dalton et al.[16] developed a different approach to synthesize polyimide second-order NLO materials. Significant enhancement in stability has been made due to the high glass transition temperature. We recently synthesized a new nonlinear optical chromophore which allows us to synthesize a new poly(amic acid) (Scheme 1). This poly(amic acid) can be easily cast into optical quality films and be imidized by thermal treatment to generate a polyimide with a high glass transition temperature. A very large and exceptionally stable second harmonic generation (SHG) coefficient was observed. This paper reports the synthesis and physical characterization of this new polyimide.

The key step in synthesizing this polymer is the synthesis of a new NLO chromophore bearing two aliphatic amino groups. As shown in Scheme 1, the amino groups were introduced into two arms of the chromophore utilizing the Mitsunobu reaction from a corresponding dihydroxyl chromophore (compound 1). It was found that the Mitsunobu reaction transformed the hydroxyl groups smoothly into phthalimides in a reasonable yield. In general, the following hydrazinolysis of the phthalimide was carried out in an ethanol solution to generate amino moieties. Due to the poor solubility of compound 2 in ethanol, we chose THF as solvent. The experimental results showed that compound 2 can be readily dissolved in THF and the hydrazinolysis proceeded in high yield. Spectroscopic data and elemental analysis support the structure as proposed.

The poly(amic acid)s from the aromatic dianhydrides with aromatic diamines or alicyclic diamines were generally

Scheme 1. Syntheses of Diamino NLO Chromophores Poly(amic acid) and Polyimide



synthesized in aprotic solvents at room temperature. The polycondensation reaction between aliphatic diamines and aromatic bis(acid anhydride)s was reported to occur only at high temperatures under high pressure. However, our reaction proceeded smoothly at room temperature. Reasonable molecular weight was obtained with an intrinsic viscosity of 0.4 dL/g.

The structure of the poly(amic acid) was confirmed by spectroscopic studies. The ^{1}H NMR spectrum of poly(amic acid) showed a change in the $-CH_2-$ proton chemical shift. The chemical shift of the methylene group linked with a primary amine was changed from 2.75 to 3.6 ppm after the formation of amide while another methylene linked with a tertiary amine was shifted only from 3.2 to 3.4 ppm. The chemical shifts due to the stilbene unit were identical with those in the monomer. Two peaks at 8.55 and 8.70 ppm were evident due to chemical shift of the amide protons. The chemical shift due to acidic protons appeared at 13.5 ppm.

The FTIR spectrum of poly(amic acid) clearly showed the bands due to the carbonyl group in an amide linkage at 1719 cm^{-1} and in a carboxylic acid at 1651 cm^{-1}. Two strong absorption bands due to the nitro group in the NLO chromophore appeared at 1337 and 1516 cm^{-1}, respectively. These results were consistent with the structure as proposed. After thermal curing, a dramatic change appeared in the FTIR spectrum. New bands appeared at 1772 (carbonyl asymmetric stretching), 1382, 1150, and 726 cm^{-1}, a typical change accompanying the imidization process. The band at 1651 cm^{-1} due to the carboxylic acid completely disappeared after the polymer film was cured at 200 °C overnight under nitrogen. However, the bands due to the nitro group on the NLO chromophore did not change appreciably in intensity, indicating that the NLO chromophore withstands the curing process. These results are consistent with observations in TGA, DSC, and UV/vis studies.

The UV/vis spectra of both poly(amic acid) and polyimide films (prepared by spin coating) exhibited a typical absorption pattern due to the aminonitrostilbene NLO

0024-9297/94/2227-2638$04.50/0

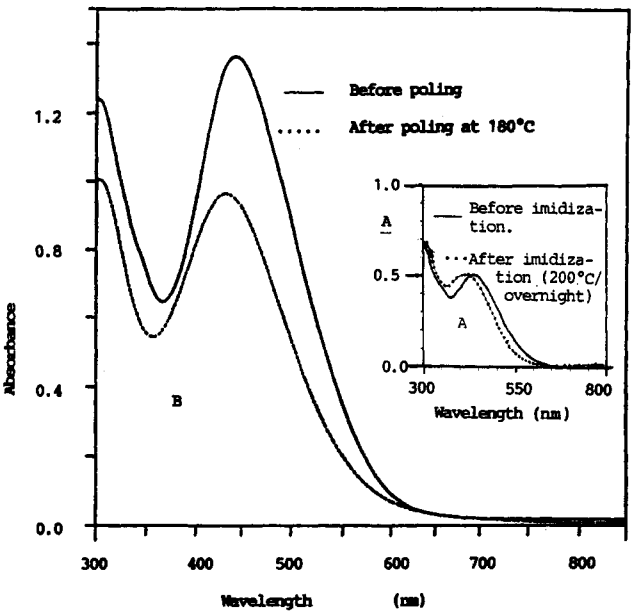


Figure 1. UV/vis spectra of poly(amic acid) and polyimide: (A) without poling; (B) with poling.

chromophore with an absorption maximum showing at ca. 450 nm (Figure 1). Samples without corona poling showed very small effect before and after imidization at ca. 200 °C. However, after poling, the dipole moment of the NLO chromophore was aligned and birefringence was introduced. The UV/vis spectrum of polyimide exhibited a decrease in absorption from which the order parameter of the poled film can be estimated. Under conditions of a 5-kV poling field (between the discharging needle and the counter electrode, ~1 cm separation) at 180 °C, an order parameter value of 0.30 was deduced. A poling field strength of 2.5 mV/cm was estimated from the order parameter.

The polyimide was thermally stable up to 350 °C under a nitrogen atmosphere, while the poly(amic acid) started to lose weight at around 150 °C due to imidization. The imidization process was completed as the temperature reached 210 °C as shown in both the TGA and DSC traces, which indicated that, to imidize a sample, the curing temperature can be set at about 200 °C under nitrogen without risk of damaging the materials. After imidization, the polyimide exhibited a glass transition temperature of 250 °C deduced from the DSC trace. It was also found that after imidization the polymer film thickness was reduced by about 10%.

Refractive indices of the polyimide were measured by using a Rudolph 43603-200E ellipsometer at several wavelengths. The results were used in fitting the Sellmyer equation to obtain refractive indices of 1.833 ± 0.002 and 1.746 ± 0.002 at 532 and 1064 nm, respectively.

The measurements of second harmonic generation were performed at a wavelength of 1064 nm. A model-locked Nd:YAG laser (continuum-PY61C-10, 25 ps, 10-Hz repetition rate) was used as a fundamental light source (1064 μm). As expected for nitro(dialkylamino)stilbene, a very large d_{33} value of 115 pm/V was obtained (with an experimental error of 20% due to laser fluctuation and the inaccuracy of the d_{11} value of the quartz standard sample). Since the second harmonic wavelength (532 nm) is in the absorptive region of the polymer, there is a large resonant contribution to the d_{33} value. It is known that, for device applications, a large nonresonant value is important. Since we do not have a longer wavelength laser source, we evaluated the nonresonant value of this material

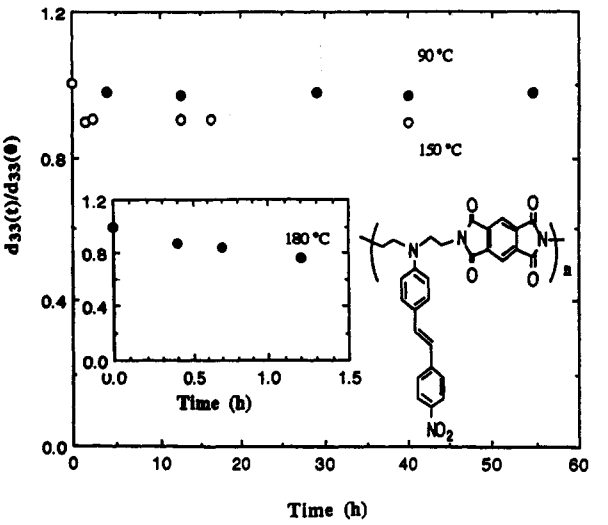


Figure 2. Temporal stability of SHG signal of the polyimide at different temperatures.

by using an approximate model, a two-level model. It was determined that the disperseless d_{33} value of the polyimide was ca. 27 pm/V.

To evaluate the high-temperature stability of our polymers, we studied the temporal stability of a second harmonic generation (SHG) signal. It was found that the SHG signal did not decay at room temperature and at 90 °C (Figure 2). When the SHG signal of the polymer film was monitored at 150 °C, an initial decay of 15% was observed and the signal was then stabilized at ca. 85% of its initial value. We further studied the stability of 180 °C and found that the decay was speeded up due to 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 period of time. After almost 1.5 h, ca. 70% of the SHG signal was retained. From these results we can see that this material is very promising for practical applications.

In summary, we synthesized a new NLO polyimide which exhibited an exceptional stability at high temperatures. The synthesis of a new diamino NLO chromophore was the key step to synthesize this polyimide, which was accomplished by utilizing the Mitsunobu reaction. Due to the versatility of the reaction scheme, many new materials can be expected.

Acknowledgment. This work was supported by the Office of Naval Research Grant N00014-93-1-0092 and by the National Science Foundation. Support from the Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award) is gratefully acknowledged.

References and Notes

(1) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; John Wiley and Sons: New York, 1991.
(2) *Materials for nonlinear optics: Chemical perspectives*; ACS Symposium Series 455; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; American Chemical Society: Washington, DC, 1991.
(3) *Nonlinear optical properties of organic molecules and crystals*; Chemla, D. S., Zyss, J.; Eds.; Academic Press: New York, 1987.
(4) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.
(5) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.
(6) Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1990**, *2*, 229.
(7) Chen, M.; Yu, L. P.; Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *Proc. SPIE* **1991**, *1409*, 202.
(8) Chen, M.; Yu, L. P.; Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421.

(9) Shi, Y. Q.; Steier, W. H.; Yu, L. P.; Chen. M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *58*, 1131.
(10) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. *Appl. Phys. Lett.* **1991**, *58*, 2459.
(11) Ranon, P. M.; Shi, Y. Q.; Steier, W. H.; Xu, C.; Wu, B.; Dalton, L. R. *Appl. Phys. Lett.* **1993**, *62*, 2605.
(12) Yu, L. P.; Chan, W. K.; Bao, Z. *Macromolecules* **1992**, *25*, 5609.
(13) Chen, M.; Yu, L. P.; Dalton, L. R.; Shi, Y.; Steier, W. *Macromolecules* **1991**, *24*, 5421.
(14) (a) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. J. *Appl. Phys. Lett.* **1991**, *58*, 225. (b) Marturunkakul, S.; Chen, J. I.; Jeng, R. J.; Sengupta, S.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1993**, *5*, 743.
(15) Lin, J. T.; Hubbard, M. A.; Marks, T. J.; Lin, W.; Wong, G. K. *Chem. Mater.* **1992**, *4*, 1148.
(16) Becker, M. W.; Sapochak, L. S.; Ghosen, R.; Xu, C. Z.; Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *Chem. Mater.*, in press.