

A Cross-Linkable Polyimide for Second-Order Optical Nonlinearities

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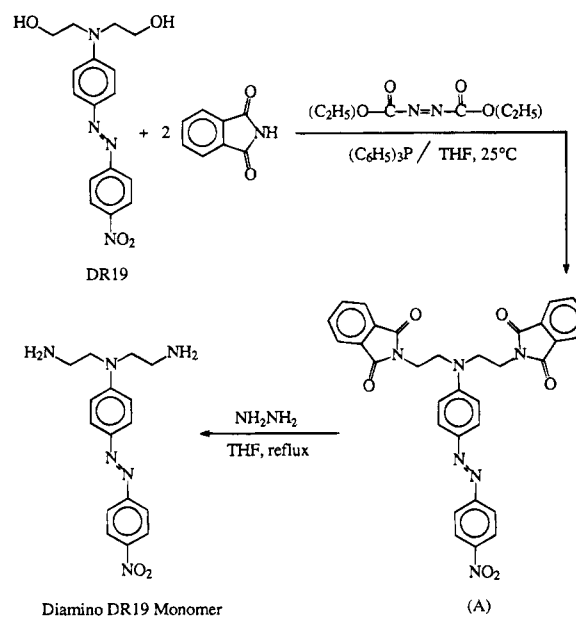
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A new cross-linkable polyimide with an NLO chromophore covalently incorporated for second-order optical nonlinearities has been developed. The prepolymer exhibited good solubility in common organic solvents, permitting processing relevant to device fabrication. Optical-quality films were obtained, efficiently poled, cross-linked and imidized. The lattice hardening due to cross-linking and imidization resulted in good stability of the poling-induced order at elevated temperatures. The second harmonic generation signal exhibited dynamic stability up to 160 °C and a d_{33} coefficient of 70 pm/V.

One of the key issues in developing electrooptic polymers for optical modulation and switching is whether the polymers have good stability. For electrooptic polymers utilizing an external electric force to achieve noncentrosymmetric ordering of the chromophores, the poling-induced order is thermodynamically unstable, especially at elevated temperature. Various approaches have been used to harden the noncentrosymmetric lattice to stabilize the poling induced order.¹ Two of the most promising approaches are (1) cross-linkable polymer systems²⁻⁵ and (2) high glass transition temperature polymer systems such as polyimides.⁶⁻⁹

The first use of polyimides as nonlinear optical materials was in guest/host systems.^{10,11} These systems suffered from three major problems: (1) rapid relaxation of poling-induced order, (2) poor loading of the chromophores, and (3) sublimation of the chromophores. To address these problems, Marks et al.,¹² Dalton et al.,⁸ and Yu et al.⁹ covalently incorporated chromophores into

Scheme 1. Syntheses of NLO Diamino Chromophore



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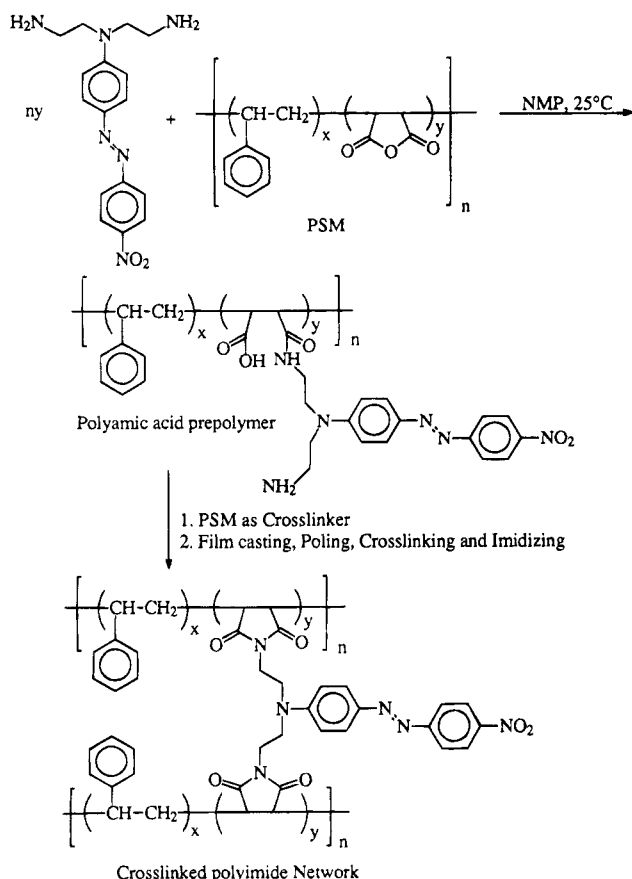
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polyimides and achieved better NLO thermal stability and nonlinearities. However, the poor solubility of many polyimides in common organic solvents makes it difficult to obtain good films. We report here the preparation of a cross-linkable polyimide system where NLO chromophore DR19 was covalently incorporated into the polymer as a pendent group. The NLO properties and thermal ramping stability (referred to as the "dynamic" stability) of the material are also presented. The reaction scheme for the synthesis of the material is given in Schemes 1 and 2. The advantage of this approach is that the prepolymer backbone before cross-linking is more flexible than polyamic acid and thus more soluble in common organic solvents, allowing a larger processing window, yet retaining the stability of polyimides.

Scheme 2. Syntheses of Cross-Linked Polyimide

4-[Bis(2-phthalimidylethyl)amino]-4'-nitroazobenzene (Compound A). Disperse red 19 (DR19), 2,2'-{4-[(4-nitrophenyl)azo]phenyl}iminobisethanol, was synthesized according to literature procedure.¹³ Diethylazodicarboxylate (DEAD) (3.50 g, 20.0 mmol) in THF (12 mL) was added dropwise into a solution of DR19 (3.31 g, 10.0 mmol), triphenylphosphine (5.52 g, 20.0 mmol), and phthalimide (3.00 g, 20.0 mmol) in THF (25 mL). The resulting mixture was stirred overnight. THF (10 mL) was added to dissolve the side products and the red product precipitated out. The red solid was collected by filtration, washed with hot methanol and recrystallized from chloroform/hexane to yield compound A, 4.54 g (77.1%). ¹H NMR (CDCl₃, ppm) δ from TMS 3.80 (t, $J = 6.5$ Hz, 4H, -NCH₂-), 3.98 (t, $J = 7.2$ Hz, 4H, -CH₂NCO-), 7.04 (d, $J = 9.0$ Hz, 2H, aromatic protons), 7.70 (m, 4H, phthalimide protons), 7.84 (m, 4H, phthalimide protons), 7.89 (d, $J = 9.0$ Hz, 2H, aromatic protons), 7.95 (d, $J = 9.0$ Hz, 2H, aromatic protons), 8.34 (d, $J = 9.0$ Hz, 2H, aromatic protons). Anal. Calcd for C₃₂H₂₄N₆O₆: C, 65.30; H, 4.11; N, 14.28; O, 16.31. Found: C, 65.18; H, 4.14; N, 14.50.

4-[Bis(2-aminoethyl)amino]-4'-nitroazobenzene (Diamino DR19 Monomer). To a three-neck flask containing compound A (4.54 g, 7.71 mmol) and THF (160 mL) was added 30 mL (large excess) hydrazine hydrate. The mixture was refluxed overnight under argon; then it was cooled to room temperature and transferred to a separatory funnel. The bold THF layer was separated, and THF was removed by ro-

tavaporization. The dark red solid residue was recrystallized from MeOH/water to yield the diamino monomer 1.50 g (59.2%). ¹H NMR (DMSO-*d*₆, ppm) δ from TMS 1.70 (br, 4H, amine protons), 2.72 (t, $J = 7.0$ Hz, 4H, -CH₂NH₂), 3.43 (t, $J = 7.0$ Hz, 4H, -CH₂N<), 6.89 (d, $J = 9.2$ Hz, 2H, aromatic protons), 7.78 (d, $J = 9.2$ Hz, 2H, aromatic protons), 7.90 (d, $J = 9.2$ Hz, 2H, aromatic protons), 8.32 (d, $J = 9.2$ Hz, 2H, aromatic protons). ¹³C NMR (DMSO-*d*₆, ppm) δ from TMS 54.45, 111.79, 122.84, 125.33, 126.40, 142.73, 146.88, 152.41, 156.64. Anal. Calcd for C₁₆H₂₀N₆O₂: C, 58.52; H, 6.14; N, 25.59; O, 9.74. Found: C, 58.06; H, 6.10; N, 25.12.

Polyamic Acid Prepolymer. The attachment of the diamino chromophore to the poly(styrene-co-maleic anhydride) (PSM) was carried out in a drybox at room temperature. PSM (75 wt % styrene, 41.0 mg, 0.4 mmol) was added to the diamine (34.2 mg, 0.1 mmol) dissolved in 1.0 mL of 1-methyl-2-pyrrolidinone (NMP). After 3 h, the resulting solution was used to prepare films directly. To characterize the prepolymer, the prepolymer was precipitated into chloroform and collected by filtration. The prepolymer was washed in a Soxhlet extractor using chloroform under argon and then dried in a vacuum. The prepolymer was a dark red powder and is soluble in common organic solvents such as THF and DMF.

Film Fabrication and Characterization of the Polymer

The NMP solution obtained according to the procedure described above was mixed with 0.5 mL of PSM/THF (2.05 g in 25.00 mL) solution. The PSM was used as a cross-linker. The mixture was filtered through a 0.2 μ m Teflon membrane filter and subsequently spin cast onto indium-tin oxide (ITO) coated glass slides. Crack-free films with thicknesses of 0.5–2.3 μ m were frequently obtained. If the films were not spun immediately, the solution gelled in 30 min because the cross-linking reaction occurs at room temperature in solution. However, the cross-linking reaction is much slower in the dried thin films. This is because the cross-linker PSM is a polymer, which requires a temperature close to or above its crystalline melting temperature (T_m) to become sufficiently mobile for the reaction to occur. The films were dried in vacuum at room temperature overnight and then at 90 °C overnight to remove the residual solvent. The films were corona poled using the ITO as the ground plane.¹⁴ To achieve optimum poling efficiency and cross-linking density, the films were poled according to a multistep poling schedule: 50–120 °C, 8 min; 120 °C, 60 min; 120–160 °C, 8 min; 160 °C, 90 min; 160–220 °C, 10 min; 220 °C, 30 min. In this schedule, the films were kept at 120 °C for 1 h to let the cross-linking reaction occur, because PSM has a T_m of 122 °C. Then the films were left at 160 °C for 90 min because the imidization starts at 160 °C. Finally the films were heated to elevated temperature (220 °C) for 30 min to complete the imidization. A corona voltage of 6 kV was applied on the films during the entire processes. The cured films were very tough and resistant to organic solvents including NMP, *N,N*-dimethylacetamide (DMAc), THF, chloroform, etc. The imidiza-

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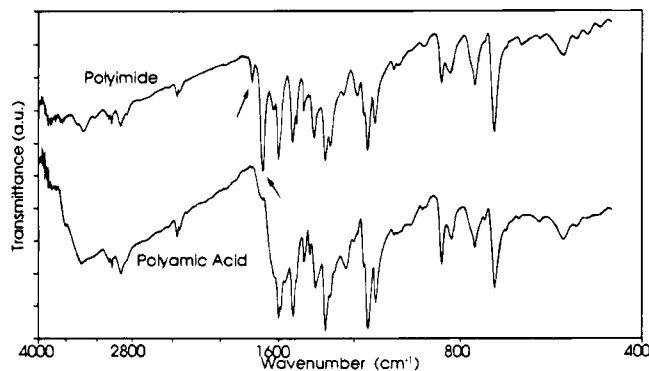


Figure 1. FT-IR spectra of polyamic acid and polyimide. The arrows indicate that new bands appeared due to the formation of imide group.

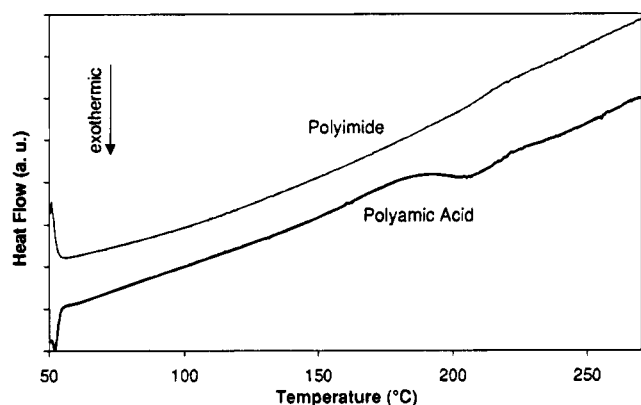


Figure 2. DSC traces of polyamic acid and polyimide. Heating rate is 10 °C/min.

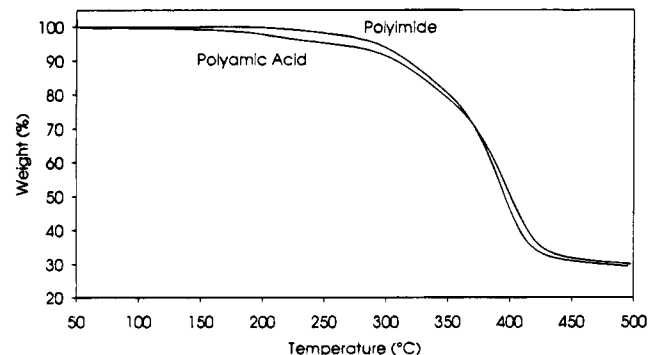


Figure 3. TGA traces of polyamic acid and polyimide. Heating rate is 5 °C/min.

tion process was monitored using FT-IR. New peaks at 1770 and 1700 cm^{-1} that are characteristic bands of the imide group appeared after imidization (Figure 1).

DSC and TGA traces of the polyamic acid also provide evidence of the imidization process. The DSC trace of the polyamic acid showed a glass transition temperature (T_g) at ca. 195 °C. This thermal transition was not observed in the DSC scan of the cured polymer, indicating the imidization was complete. TGA traces showed that the loss of water during imidization corresponds to a ~4% weight loss, which agrees with the theoretically expected value (Figures 2 and 3).

In Figure 4 the UV–near-IR absorption spectra of the cross-linked polymers, with and without poling, are shown. The bold spectrum was obtained with a film treated with the heating profile described above but without any electric field applied. The light spectrum was obtained with a film treated with the same profile

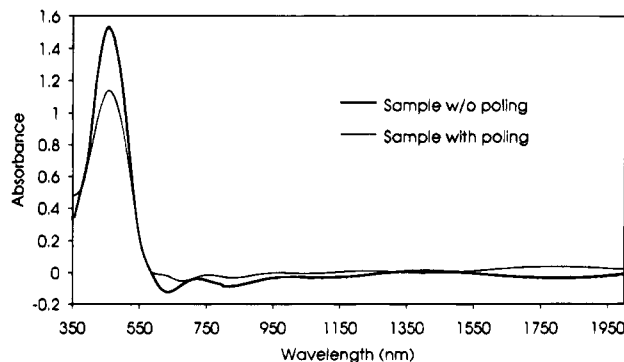


Figure 4. Ultraviolet–near-IR spectra of cross-linked polyimides with and without poling. Away from the resonance peak, the negative absorbance values with respect to an uncoated reference substrate are due to Fabry–Perot interference effects in the film.

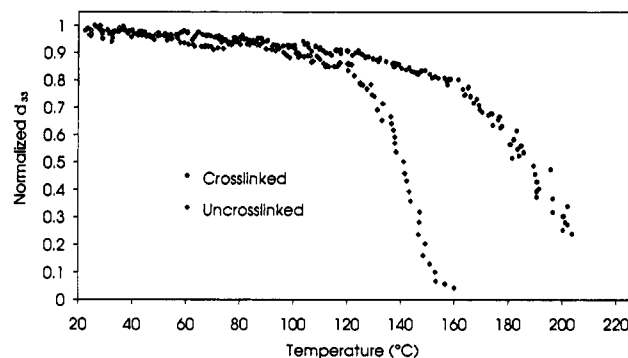


Figure 5. Dynamic stability of NLO activity of the cross-linked polyimide and un-cross-linked polymer. Heating rate is 10 °C/min.

and with the electric field on. Using these procedures, the bleaching at ~480 nm caused by high temperature is eliminated from the data. The absorption peak is due to the intramolecular charge-transfer band of the NLO chromophores. The decrease of the peak absorbance is caused by alignment of chromophore dipoles along the poling field direction, which is the incident light direction as well. From the absorbance change, the ordering parameter of the poled films were determined to be 0.26.

The second-order NLO properties of the films were characterized by second harmonic generation (SHG) at 1064 nm fundamental wavelength, with a quartz crystal ($d_{11} = 0.5 \text{ pm/V}$) as the reference. The measurements were taken after the poled films were left at room temperature overnight to remove the residue charge caused by the poling field. For the cross-linked polymer, a SHG d_{33} coefficient of 70 pm/V was obtained. This moderate value may be accounted for by the relatively low loading density of 26% of the NLO chromophore incorporated in the polymer.

The dynamic thermal stability of the NLO activity of the cross-linked polymer and un-cross-linked polymer films (without added PSM) are shown in Figure 5. The study of the real time NLO stability of the polymer films as a function of temperature provides information on maximum device processing temperature that the film can withstand and allows quick evaluation of the temporal and thermal stability of the material. From our experience, materials will have long-term stability at temperatures approximately 30 °C below the temperature where the NLO activity starts to decrease.⁷ Clearly the cross-linked film exhibited greater stability.

Note that the imide groups in the un-cross-linked polymer are not on the polymer backbone but on the pendent groups. This may account for the lower stability than other un-cross-linked polyimides.^{8,9} The dramatic improvement in thermal stability of the cross-linked polymer is due to (1) cross-linking and (2) imidization which incorporated the imide groups into the polymer backbone.

In conclusion, we have prepared a processible cross-linked polyimide where NLO chromophores were covalently incorporated into the system. The material demonstrated good thermal stability and a large SHG signal. The synthesis scheme can be extended to prepare other polymers with better NLO properties. Work is underway to increase the loading density of the chromophore and introduce another amine group on the

electron-withdrawing side of the chromophore for imidization and cross-linking to lock in the poling-induced order. Some higher β chromophores are being synthesized and will be incorporated into the cross-linkable polyimide system.

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