Large and Stable Nonlinear Optical Effects Observed for a Polyimide Covalently Incorporating a Nonlinear Optical Chromophore

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In the search for poled polymeric materials for devices utilizing second-order nonlinear optical effects, such as electrooptic modulators and frequency doublers, one must consider the stability of the poling-induced noncentrosymmetric order of the materials. Poling-induced order is thermodynamically unstable and tends to relax to the more stable random structure in the absence of the poling electric field, especially at elevated device working temperatures (60–125 °C). This relaxation of structure leads to the decay of the second-order optical nonlinearity.

Various approaches have been used in the attempt to stabilize the poling-induced order. These approaches include cross-linkable polymer systems[1–13] and high T_g polymers.[14–21] The most studied high-T_g polymers for nonlinear optical (NLO) device applications are polyimides, which have been used either as polymer hosts[16–19] for composite NLO materials or as polymer backbones for side-chain NLO chromophores.[20,21]

Wu et al. pioneered the use of polyimides as high-T_g polymers by using the polyimides as hosts for composite NLO materials.[16] After electrically poling and thermally curing a polyamic acid (the polyimide precursor) film doped with an NLO-active chromophore, NLO stability at 150 °C was attained. However, the electrooptic coefficients of these systems were not very large, and bleaching of the films has been observed at high poling and curing temperatures, as indicated by the disappearance of the major charge-transfer absorption peak. Similar bleaching has been observed in other polyimide composite systems as well.[19] Other problems associated with the polyimide–chromophore composite systems include the limitation of effective chromophore loading due to incompatibility between the polymer host and the chromophore guest, the sublimation of low molecular weight chromophores at prolonged high working temperatures, and the extraction of dye molecules by organic solvents encountered in building multilayer devices with the solution casting method. To address these problems, Marks and co-workers focused on covalent incorporation of chromophores into polyimide structures.[21] By attaching a nitroaniline derivative to the polyimide backbone as a pendant, they attained moderate nonlinearities stable at 85 °C.

Along with stability of the second-order nonlinearities, one must maximize various factors in the polymer system in order to make it device applicable. These factors include using a chromophore with a large molecular hyperpolarizability (β) and achieving adequate number density of the chromophore within the polymer which yields reasonable poling efficiency. Thus, focus must be on designing systems with large bulk optical nonlinearities (through increasing loading density of large-β chromophores and maintaining good electric field poling efficiency) and high NLO stability.

We report here the use of a polyimide system into which disperse red 19 (DR19) is covalently incorporated into the polymer. The resulting high-T_g material exhibits excellent long-term stability of the large second-order optical nonlinearities at elevated temperatures. The reaction scheme for the synthesis of the polyimide is given in Scheme 1.

DR19, the synthesis of which is described elsewhere,[9] was added to a solution of trimelletic anhydride acid chloride in *N*-methylpyrrolidinone (NMP) at 0 °C. Cold pyridine was then added to neutralize the HCl created during the reaction. The reaction was allowed to continue at room temperature for 2 h. The product was recrystallized from acetic anhydride and dried at 150 °C under vacuum overnight yielding monomer I, 93%, mp 272–274

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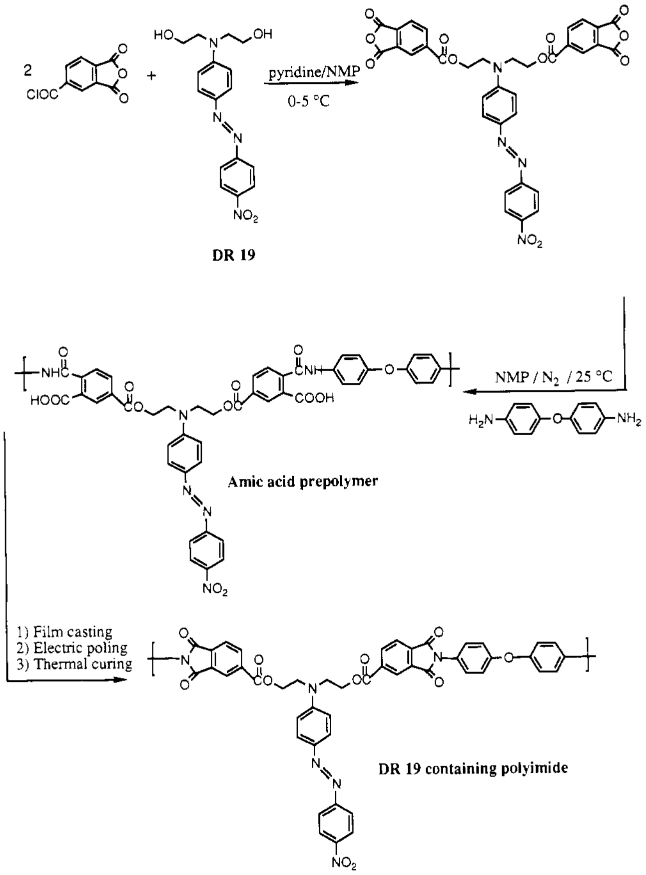
Scheme 1. Reaction Scheme for Synthesis of DR19 Containing Polyimide



°C, ^{1}H NMR ($CDCl_3$) δ 4.06 (t, 4 H, J = 4Hz), 4.61 (t, 4 H, J = 4 Hz), 7.17 (d, 2 H, J = 9 Hz), 7.82 (d, 2 H, J = 9 Hz), 7.93 (d, 2 H, J = 9 Hz), 8.15 (d, 2 H, J = 9 Hz), 8.38 (m, 6 H, J = 9 Hz). Anal. Calcd for $C_{34}H_{22}N_4O_{12}$: C, 60.18; H, 3.27; N, 8.26. Found: C, 60.24; H, 3.24; N, 8.27.

The polymerization was carried out in a drybox at room temperature. The diamine was dissolved in NMP, and a stoichiometrically equivalent amount of monomer I was added over 1 h. The polymerization was allowed to continue for 5 h from the time the last amount of monomer I was added. The polymer solution was poured into chloroform, and the polymer precipitate was collected by filtration and washed with chloroform. The polymer was further purified by extraction in a Soxhlet extractor and dried under vacuum overnight yielding the polyamic acid: 74%. Anal. Calcd for $C_{46}H_{34}N_6O_{13}$: C, 62.87; H, 3.90; N, 9.56. Found: C, 62.61; H, 4.02; N, 9.38.

Initially, the polyamic acid precursor, having a lower T_g and higher solubility in common organic solvents than the final polyimide, was prepared. An NMP solution containing the precursor polymer was spin cast into thin films. These films were subsequently baked at 70 °C under vacuum for 24 h to remove the residual solvent. Typical film thicknesses were approximately 0.8-μm as measured with a Dektak IIA profiler. The films were poled using an ITO-grounded corona setup. The films were then heated at 220–250 °C for 2 h to complete imidization. The resultant polyimide has a T_g around 205 °C and is only slightly soluble in highly polar solvents. The imidization process was followed by using FTIR and NMR. New FTIR peaks at 1778 and 720 cm^{-1} that are characteristic bands of the imide carbonyl group and imide ring, respectively, in polyimides were observed after imidization. The disappearance of the NMR proton chemical shifts of the carboxylic acid and amide groups at 12.6 and 10.5 ppm, respectively, was also observed as the imidization occurred. There is no decrease in the other NMR peak intensities or peak integrations indicating that there is no chromophore degradation during the poling process. The poled and cured films exhibit large second-order optical nonlinearities; d_{33} coefficients measured by second harmonic generation (SHG) at the 1064-cm^{-1} fundamental wavelength are 2.8 × 10^{-7} esu. The ordering parameter Φ is 0.25 as calculated from the absorbance change after poling as observed in Figure 1. The decrease in absorbance after poling is an indicator of the dipole alignment and not due to chromophore degradation. These large SHG coefficients are apparently facilitated by the large weight fraction (36%) of the incorporated chromophore and resulting high poling efficiency.

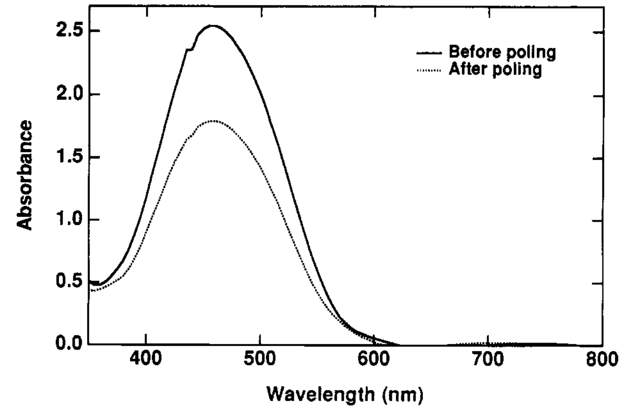


Figure 1. Absorption spectra of DR19 polyimides before and after poling at 250 °C.

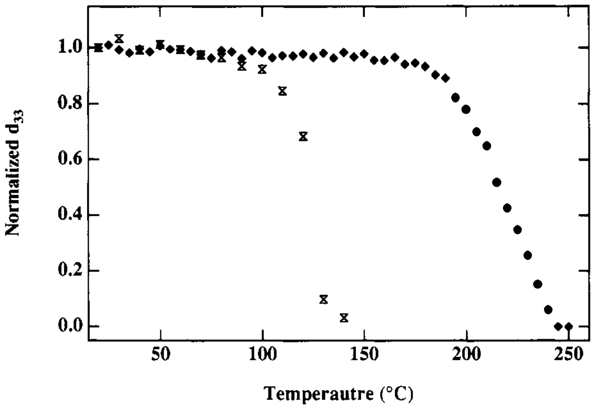


Figure 2. Normalized d_{33} coefficients of nonimidized (crosses) and imidized (diamonds) NLO polymers as a function of ramping temperature at a heating rate of 10 °C/min.

In Figure 2 we present the dynamic thermal stability of the NLO activity of the film before and after thermal curing. To study the real-time NLO stability of polymer films as a function of temperature (which provides the information of maximum device processing temperature that the film can withstand and allows quick evaluation of temporal and thermal stability of the material), in situ SHG measurements are performed before and after the imidization process at a heating rate of 10 °C/min. The configuration of the in situ SHG measurement is given in Figure 3. The film temperature is controlled by the current flow of an external power supply through the ITO layer on the back side of the glass substrate to avoid possible charge injection effects. A thermocouple anchored to the

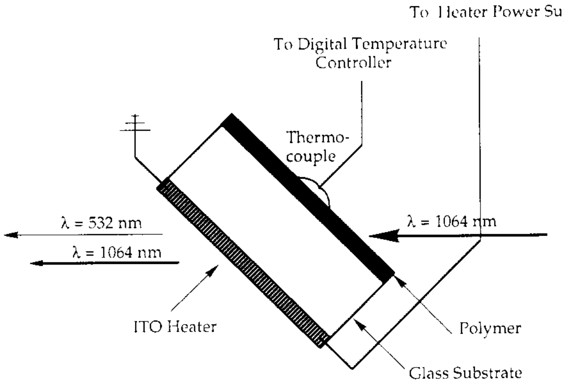


Figure 3. Configuration for the measurement of real-time dynamic thermal stability of NLO activity using the indirect heating method.

polymer film is used to monitor the film temperature. The temperature ramping rate can be controlled by an Omega CN6081 ramp-soak temperature controller. The experimental error of temperature reading is ±3 °C. The SHG signal and the temperature are recorded with a chart recorder. Clearly the cured film exhibits greater stability; no significant SHG decay is observed below 185 °C. This dramatic improvement in thermal stability of optical nonlinearity is due to the T_g elevation resulting from the thermal imidization.

In Figure 4 we present the temporal stability of the cured polyimide in which there is no negligible decay of the d_{33} signal over hundreds of hours. We are currently extending thermal stability measurements to 125 °C.

In conclusion, we have synthesized a chromophore-functionalized polyimide which when poled and cured demonstrates excellent temporal stability of the large SHG signal at elevated temperatures for hundreds of hours. The polyimide system has a high loading density of a chromophore with a good molecular hyperpolarizability, good poling efficiency, and no chromophore degradation or loss during the curing process. The synthesis presented here is a generalized scheme and other polymers are in the process of being made and the second-order nonlinear optical properties will be measured and reported shortly.

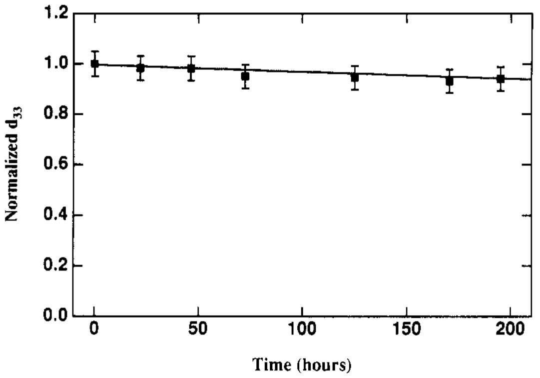


Figure 4. Temporal NLO stability of polyimide at 90 °C in air. Normalized d_{33} as a function of baking time.

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