Thermosetting Polyurethanes with Stable and Large Second-Order Optical Nonlinearity

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ABSTRACT: A two-component, thermally-curable second-order nonlinear optical material, based on polyurethane, is developed. Tough, chemically-inert films were prepared from this material. Resonance-enhanced second-harmonic generation coefficients (d_{33}) of approximately 120 pm/V at a 1.064-μm fundamental wavelength were obtained. Using a Mach-Zehnder interferometer, an electrooptic coefficient of r_{13} = 13 pm/V was measured at a 633-nm wavelength with a 3-kHz modulation frequency, which is in good agreement with that derived from the SHG d_{31} ($d_{31} = d_{33}/3$) coefficient employing a two-level model. Second-harmonic generation (SHG) revealed a long-term stability of dipole orientation in an electrically-poled and thermally-cured film. The dipole alignment of the poled and thermosetted film showed no detectable relaxation at room temperature for over 3000 h, as monitored by SHG measurement. A high poling stability was also observed when the film was kept in an oven at 90 °C for 3000 h, and 70% of the signal still remained. The versatility of the reaction scheme and the ease of processing makes this material appropriate for further development for device application.

I. Introduction

Although the advantages of second-order, nonlinear optical (NLO) polymers have been recognized and extensive efforts have been focused on this field, problems, such as relaxation of dipole orientation, phase mismatching, and optical losses,[1-10] still exist. Among them, the relaxation of dipole orientation induced by an electrical field is critical. Since most of the polymeric composite materials (guest/host) doped with NLO molecules suffer from rapid decay of NLO activity after electrical poling, they cannot be used in practical devices.[1-5] Polymers with covalently bonded NLO chromophores exhibit improved stability, but their NLO activities still decay significantly at room temperature.[1-10] Considering the fact that the most probable device application of NLO polymers is in hybrid structures with semiconductor substrates where some of the processes may require a higher temperature, the thermal relaxation observed for the above-mentioned materials is even more severe.[6]

Recently, encouraging results dealing with this issue have appeared; systems such as epoxy oligomers,[7] photo-cross-linked systems,[8,9] and even high-temperature treated polyimide composite films[10] have been reported to stabilize second-order optical nonlinearities. A certain degree of success has been achieved in these systems, which gives us inspiration to further explore new systems with improved properties. In this paper we report our recent results of thermosetting polyurethanes with large and stable second-order optical nonlinearities.

II. Experimental Section

Monomers and Materials. 4,4'-Diisocyanato-3,3'-dimethoxydiphenyl (1) was purchased from Pfaltz & Bauer (Stamford, CT) and was further purified either by sublimation or by recrystallization from hexanes before use. Dioxane was distilled from calcium hydride and was stored under an argon atmosphere. Chloroform was purified using an active alumina (activity I) column to remove a trace amount of ethanol. Disperse Red 19 was prepared according to the procedure described previously.[6] Before polymerization, the glassware was dried in an oven at 140 °C overnight and was then blown with argon gas.

Synthesis of the Prepolymer. Disperse Red 19 (0.001 mol, 0.3300 g) and compound 1 (0.002 mol, 0.5926 g) were added to dioxane (10 mL) in a three-necked flask, and triethylamine (0.1 mL) was added as a catalyst. The resulting mixture was heated to reflux for 2 h under an argon atmosphere. The solvent was pumped out, and a solid prepolymer was obtained and was stored under an argon atmosphere.

Preparation of Thin Films for Thermal Setting. Triethanolamine was used as the cross-linking agent (0.5200 g/25 mL in dioxane). The prepolymer (0.5000 g) and triethanolamine (2.59 mL) were dissolved in dioxane/chloroform (70/30, v/v). The solution was then filtered through a 0.2-mm filter and spin-cast onto transparent glass substrates with an ITO (indium tin oxide) conductive layer as the poling electrode. The polymer films were dried either in a drybox or under vacuum for 2 days. The thickness of the film, which varied from 0.1 to 3 μm, was measured with a Rudolph 43603-200E ellipsometer and a Dektak II profile.

Thermosetting and Poling. The film obtained was heated to about 160 °C while corona-poled with an intense dc electric field. The poling conditions are as follows: temperature, 160–200 °C; high voltage, 12–14 kV at needle point; poling time, 60 min; gap distance, ca. 1.5 cm; poling current, <0.1 mA. After thermal setting, the polymer film was cooled down to room temperature in the presence of the electrical field.

Characterization of the Prepolymer and the Polymer. The concentration of unreacted isocyanate groups in the prepolymer was determined by the FTIR method.[11] Dioxane was used as the solvent, and the following concentrations of 4,4'-diisocyanato-3,3'-dimethoxydiphenyl were prepared to obtain a standard calibration curve: 4×10^{-5}, 3.2×10^{-5}, and 2×10^{-5} mol/5 mL. A salt plate cell ($11 \times 30 \times 7$ mm^3) was used to obtain the spectrum. The path length of the solution in the cell is 1 mm. The cell was flushed with dry acetone and then dried with argon before use. The spectrum was taken in a frequency range between 2700 and 1800 cm^{-1}. The spectrum of a dioxane solution of the

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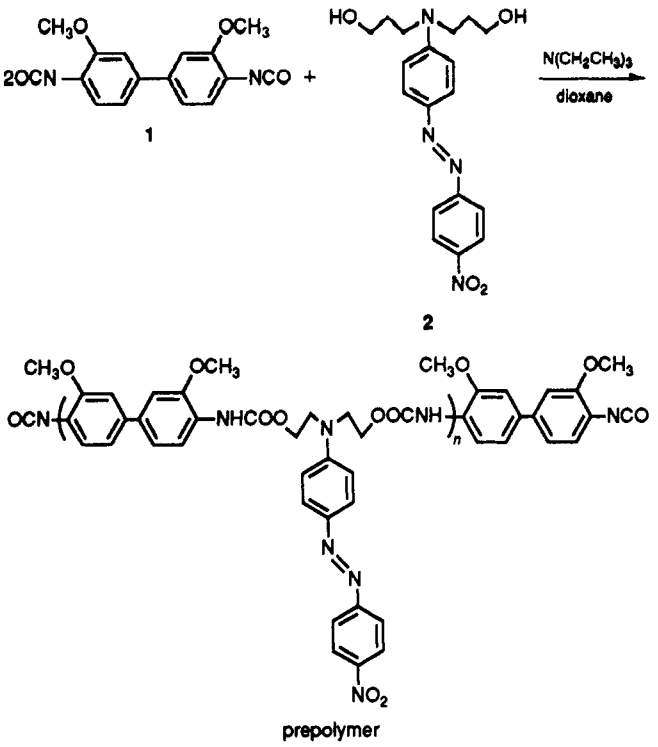
Scheme I
Synthesis of the Prepolymer



prepolymer (3.00×10^{-5} mol/5 mL) was recorded under the same conditions.

FTIR spectra were taken with a Perkin-Elmer FTIR spectrometer. Thermal analyses were performed using Perkin-Elmer DSC-7 and TGA-7 systems with a heating rate of 10 °C/min. Viscosity measurements were performed employing a Ubbelohde viscometer.

NLO Measurement. The second-harmonic measurements were performed according to the procedure reported previously.[8] A Spectra-Physics DCR-11 Q-switched Nd:YAG laser with a pulse width of <10 ns and a 10-Hz repetition rate was used as a fundamental source. The film of the polymer sample was held at a 45° angle to the incident laser beam. A quartz crystal was used as a reference sample, and second-order NLO susceptibility was thus calculated according to known procedures.[1]

The electrooptic coefficient (r_{13}) of a poled sample was measured with a Mach-Zehnder interferometer setup. The polymer sample was coated on the gold thin layer. The laser beam propagated through the poled film at a normal incidence so that only r_{13} was involved in this measurement.

III. Results and Discussion

The reaction approach is shown in Scheme I, where 4,4′-diisocyanato-3,3′-dimethoxydiphenyl was chosen as the monomer because it was not very sensitive to the moisture. Another reason to choose 4,4′-diisocyanato-3,3′-dimethoxydiphenyl as the backbone is that the biphenyl units can increase the rigidity of the polymer chain. To accelerate the reaction, triethylamine (1%) was used as a catalyst. The prepolymer was collected after pumping out all of the solvent. In order to add the correct amount of the cross-linking agent, a precise percentage of the unreacted isocyanate group in the prepolymer was determined. It is well-known that the isocyanate group has a well-resolved absorption peak at ca. 2200 cm^{-1}.[12] Therefore, we utilized FTIR to determine the amount of unreacted isocyanate groups in the prepolymer. Base-line absorbances of the isocyanate groups at 2234 cm^{-1} were precisely measured as a linear function of the number of –NCO groups in a given weight of compound 1 (see Figure 1). The absorption intensity of the isocyanate groups of the prepared prepolymer solution was controlled within 0.14–0.34, and the concentration of the remaining –NCO groups was calculated against the calibration curve.

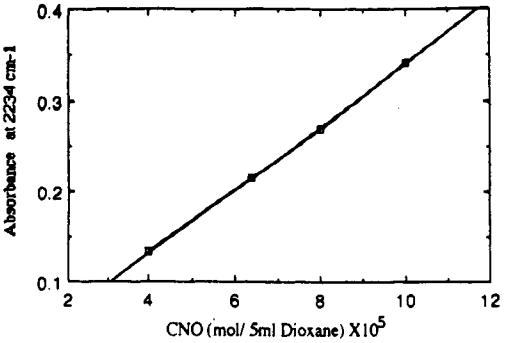


Figure 1. Standard calibration curves of –NCO groups.

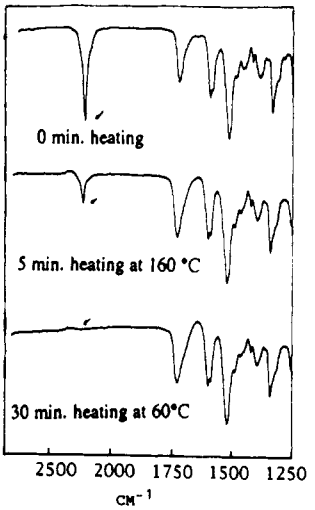


Figure 2. FTIR spectra of pristine oligomer and cured materials.

If all of the hydroxyl groups of Disperse Red 19 reacted with isocyanate groups, the remaining isocyanate groups would be half of the starting concentration. The absorbance of a prepolymer solution, which theoretically amounts to 6.0 mol of –NCO group/5 mL, was measured as 0.193, corresponding to the remaining CNO of 5.80 mol/5 mL. The reactivity was estimated to be 97%. Because there is no hydroxyl group resonance found in the ^{1}H-NMR spectrum, the prepolymer must be terminated by isocyanate groups. The prepolymer is soluble in dioxane and DMF. Viscosity measurement showed an intrinsic viscosity of ca. 0.02 dL/g using *N*-methylpyrrolidone as solvent, indicating a low molecular weight oligomer.

To carry out further cross-linking, two trifunctional compounds have been studied, glycerol and triethanolamine. It was found that glycerol has a poor solubility in both dioxane and chloroform. However, triethanolamine is a better compound as a cross-linking agent due to its greater solubility. Thus, a stoichiometric amount of the prepolymer (–NCO/–OH = 1/1) and triethanolamine were mixed to form a clear solution which was then cast into thin films. After the thin film was annealed above 160 °C for about 30 min, an extremely stable, tough, chemically-inert, and optical-quality film was formed, which clearly indicates that the cross-linking did happen. FTIR spectra provided further evidence; as shown in Figure 2, after the prepolymer was heated at 160 °C for 5 min, the absorption of isocyanate group at 2241 cm^{-1} was reduced by 80% compared to the pristine film; after heating for 30 min, the isocyanate absorption peak completely disappeared while the other absorption bands, such as absorption bands of the nitro groups at 1519 and 1345 cm^{-1}, remained unchanged.

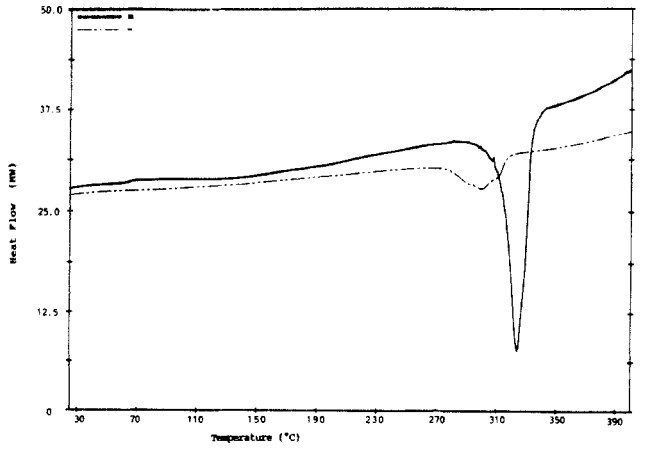


Figure 3. DSC trace of the oligomer and cross-linked materials.

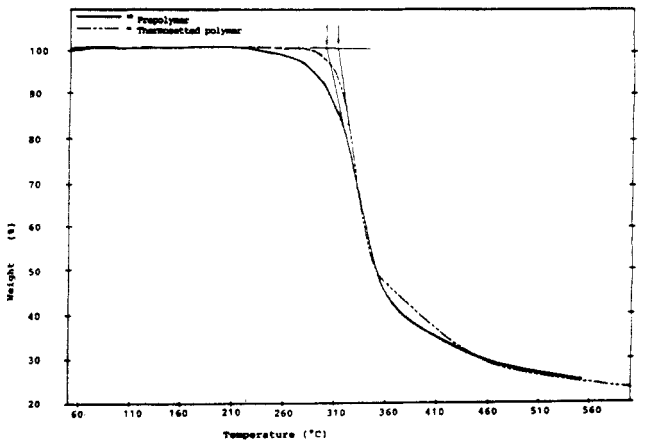


Figure 4. TGA trace of the oligomer and cross-linked materials.

The thermal properties of the prepolymer and thermosetted polymer were studied using DSC and TGA (see Figures 3 and 4). No thermal transitions have been detected between 30 and 270 °C in the DSC traces. The exothermic peaks at about 300 °C correspond to the decomposition of both prepolymer and thermosetted material, which are evidenced by TGA results. The TGA trace revealed that the prepolymer has a decomposition temperature at ca. 304 °C and the thermosetted material at ca. 316 °C as indicated in the diagram. The thermosetted polymer was more stable than the prepolymer, as indicated in the TGA diagram; no weight loss was observed on heating to 300 °C.

The thermally-cured polymer insoluble in common organic solvents, such as chloroform, dioxane, and DMF, and could only be removed by plasma oxygen etching. However, the prepolymer without addition of cross-linking agent was soluble or partially soluble in these solvents after similar thermal treatment. All of these results strongly support that the prepolymer was completely cross-linking with triethanolamine and a mesh type network was formed.

NLO Properties. Although the prepolymer is actually an oligomer, it can form smooth, optical quality thin films. An attractive feature is that the film quality became even better after thermosetting (Scheme II). The thickness of the thin film can be controlled from 0.1 to 5 μm by controlling the spin-coating speed and the concentration of the solution. A resonance-enhanced d_{33} coefficient of about 120 pm/V at a 1.064-μm fundamental wavelength was obtained by comparing with a standard quartz sample. The experimental error is about 20%, which mainly comes from the uncertainty of the reference quartz sample (ca. 10%) and the laser beam instability. With a Mach-Zehnder interferometer, an electrooptic coefficient or r_{13} = 13 pm/V was measured at a 633-nm wavelength with a 3-kHz modulation frequency, which is in good agreement with that derived from the SHG d_{31} ($d_{31} = d_{33}/3$) coefficient employing a two-level model. As we expected, the dipole alignment of the poled and thermosetted film showed no detectable relaxation at room temperature for over 3000 h, monitored by SHG measurements. Figure 5 shows the temporal behavior of the second-order nonlinear optical coefficient, $d_{33}(t)/d_{33}(0)$, as a function of the time. A high poling stability was also observed when the film was kept in an oven at 90 °C for 3000 h, and 70% of signal still remained (see Figure 6). These results indicate that these thermal-setting materials are very promising for practical applications. The following advantages can be noted in these materials: (1) The preparation of the materials is quite easy and inexpensive. (2) The materials are soluble in many common organic solvents, and optical quality films can be cast easily. (3) The synthetic reaction scheme can be extended to incorporate different NLO chromophores with multifunctional groups so that the NLO activity can be enhanced. (4) The high stability of NLO effects, especially at elevated temperature, permits fabrication of hybrid structures on semiconductor substrates.

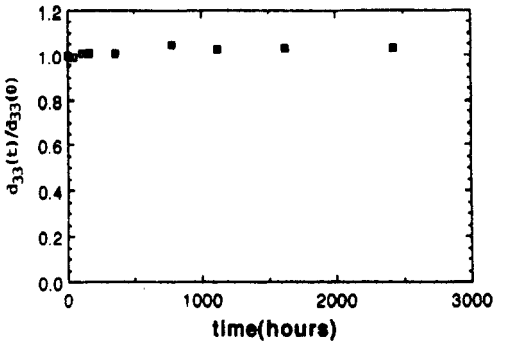


Figure 5. Temporal behavior of a second-order nonlinear optical coefficient, $d_{33}(t)/d_{33}(0)$, at room temperature.

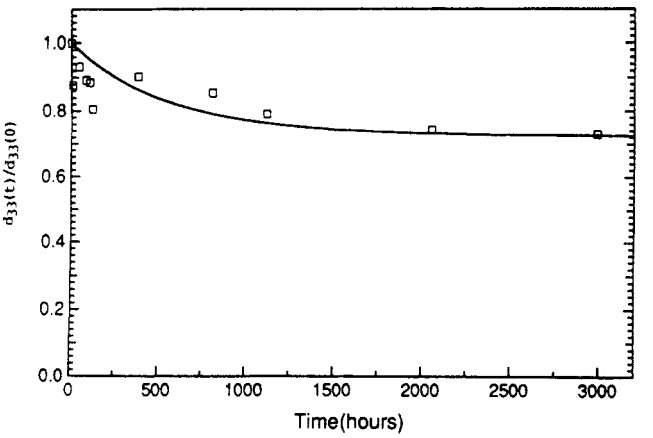
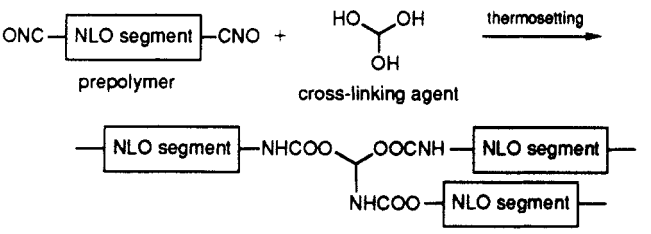


Figure 6. Temporal behavior of a second-order nonlinear optical coefficient, $d_{33}(t)/d_{33}(0)$, at 90 °C.

Scheme II
Thermal Setting of the Prepolymer



IV. Conclusion

A thermally-curable polyurethane with large and stable second-order NLO activity was developed. Tough, chemically-inert, optical quality films were prepared from this material. Second-harmonic generation revealed a long-term stability of dipole orientation in electrically-poled and thermally-cured films even at 90 °C. The versatility of the reaction scheme and the ease of processing assures this material of further utilization.

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