A Heterocyclic Polymer with Thermally Stable Second-Order Optical Nonlinearity

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Heterocyclic polymers, including polyimides, are typically high-T_g polymers due to their rigid backbone, strong interactions between the polymer chains, and high degree of crystallinity or cross-linking.[1] Because of their excellent thermal stability, they are good candidates for use as second-order nonlinear optical materials.[2-14]

One problem associated with high-T_g polymers is solubility. For example, many polyimides are not soluble, and polyamic acids must be used for processing. Even polyamic acids have limited solubility in common organic solvents and polar solvents such as 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and DMSO must be used. At least polyimides can be produced via a two-step reaction. Many other polyheterocyclics, on the other hand, can be obtained only in a one-step reaction and/or by a time-consuming cyclic condensation in the solid phase or melt.[1] Thus, to obtain processible heterocyclic polymers for second order nonlinearity, one should use oligomers that are soluble in common organic solvents and can be processed into thin films. These oligomers should contain end-capped functional groups that can be thermally cured into heterocyclic polymers. The conditions of the thermal curing and poling process should be carefully controlled,
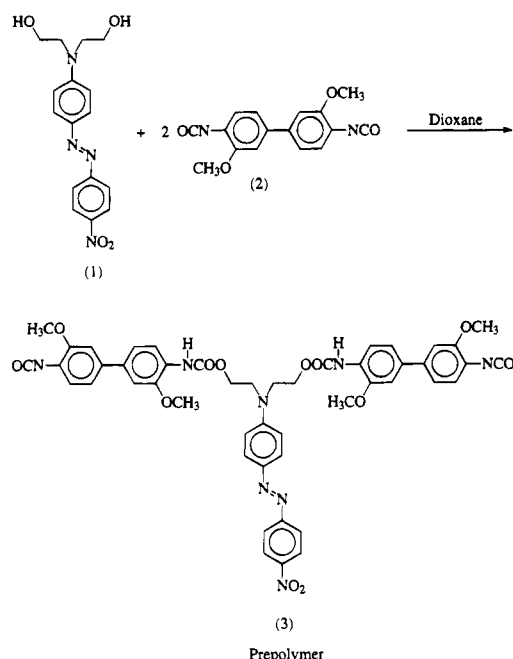

Figure 1. Synthesis scheme of the prepolymer.

because the chain growth and/or cross-linking deriving from curing not only increase T_g but also increase the fraction of as-yet-unreacted functional groups that become fixed in the network and spatially isolated. In this communication, we describe an approach employing a NLO chromophore containing prepolymer to synthesize a thermally stable heterocyclic polymer and show that the polymer can be efficiently poled. The NLO properties are also presented.

The synthetic scheme of the prepolymer is shown in Figure 1. The NLO chromophore Disperse Red 19 (**1**), 2,2′-{4-[(4-nitrophenyl)azo]imino}bisethanol, was synthesized according to literature procedures.[15] The prepolymer **3** was prepared following the literature method with some modifications. Disperse Red 19 (**1**, 0.3300 g, 1.000 mmol) and 4,4′-diisocyanato-3,3′-dimethoxydiphenyl (**2**) (0.6222 g, 2.100 mmol) were added to dioxane (10.0 mL) in a round-bottom flask. The extra amount of 5% of 4,4′-diisocyanato-3,3′-dimethoxydiphenyl was added to facilitate the formation of the prepolymer and to react with moisture if there is any. The remaining 4,4′-diisocyanato-3,3′-dimethoxydiphenyl can be removed by filtration because it does not dissolve in cold dioxane solvent. No catalyst was added to avoid cross-linking reaction of the isocyanate groups. The resulting mixture was heated to reflux for 2 h under argon. The solution was cooled to room temperature and then filtered through a 0.2 μm Teflon filter. The solvent was pumped out by a vacuum, and a red solid prepolymer was obtained. The prepolymer was stored in a drybox. The filtration step not only purified the prepolymer but also made it very easy to dissolve.

The heterocyclic polymerization scheme used to prepare poly-2-oxazolidone (**5**) is shown in Figure 2. Bisphenol A diglycidyl ether (BADGE, **4**, 0.8510 g, 2.500 mmol) was dissolved in 25.00 mL of dioxane to form a 0.100 mM solution. The prepolymer **3** (0.09229 g, 0.1 mmol)

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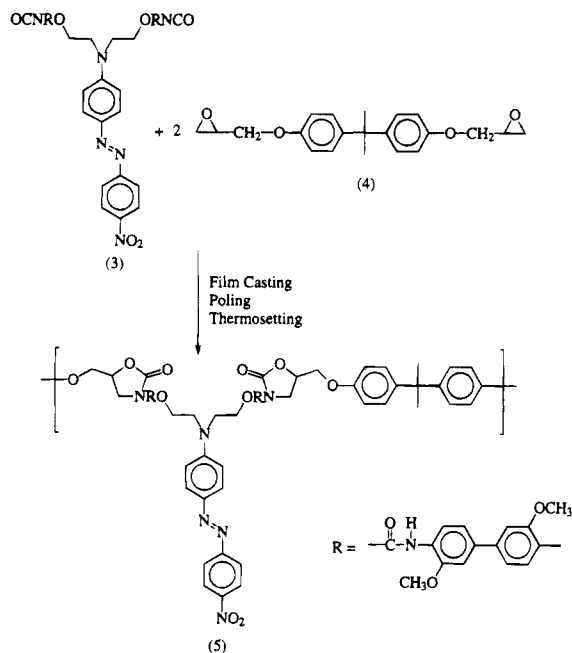(14) Liang, Z.; Dalton, L. R.; Garner, S. M.; Kalluri, S.; Chen, A.; Steier, W. H. *Chem. Mater.* **1995**, *7*, 941.

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Communications

Chem. Mater., Vol. 7, No. 10, 1995 1757

Figure 2. Synthesis scheme of the polyoxazolidone.

Figure 3. Fourier transform infrared spectra of the hetero-cyclic polymer at different polymerization stages. The arrows at 2240, 1790, and 908 cm^{-1} indicate the disappearing isocyanate group, the emerging oxazolidone, and the disappearing epoxy, respectively.

Figure 4. Ultraviolet–near-IR spectra of the heterocyclic polymer 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.

was dissolved in BADGE/dioxane solution (1.00 mL, 0.1 mmol of BADGE). The resulting solution was filtered through a 0.2 μm Teflon filter and then was spin cast onto transparent glass slides coated with an ITO conductive layer as a poling electrode. Crack-free films with a thickness range from 0.5 to 1.5 μm were easily obtained. The films were dried overnight in a vacuum at room temperature.

After the films were dried, they were poled and cured at elevated temperatures using a corona-discharge setup, with a tip-to-plane distance of 2.0 cm. The poled polymer films were cooled to room temperature in the presence of the electric field to lock in the poling-induced order. The poling voltages and temperatures, which affect both the poling efficiency and polymerization, were so selected that poling efficiency and polymerization were optimized while the film quality was preserved. To precure the prepolymer, the films were heated to 180 °C for 5 min and then cooled to 140 °C for 5 h before a corona voltage of 6 kV was applied. 1.5 h later 9 kV was applied, and poling was continued for another 13.5 h. The precuring step was necessary because the high voltage can damage the prepolymer films.

The isocyanate group in the prepolymer reacts with the epoxy group to form oxazolidone upon heating.[16] This is demonstrated by the FT-IR spectra of the prepolymer with BADGE heated at different temperatures for different periods of time as shown in Figure 3. When the prepolymer with a stoichiometrically equal amount of BADGE was heated at 120 °C for 3 h, the peak at 2240 cm^{-1} associated with isocyanate and the peak at 908 cm^{-1} associated with epoxy decreased, while the peak at 1790 cm^{-1} associated with oxazolidone appeared. After the polymer was further heated at 180 °C for 3 h, the peaks at 2240 and 908 cm^{-1} almost completely disappeared, indicating that the polymerization was nearly complete. Besides changes in those three peaks, no other change was observed in the FT-
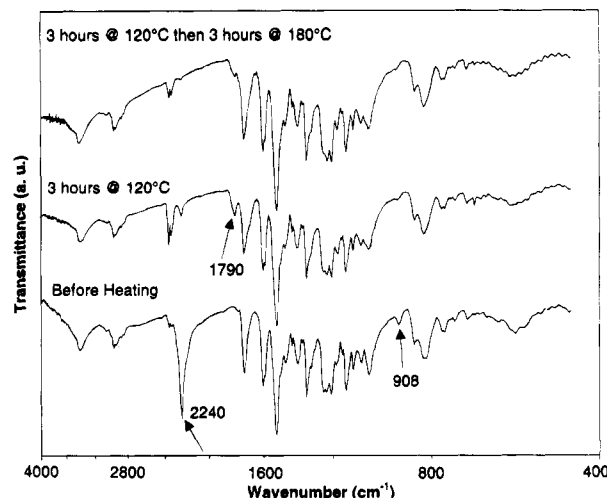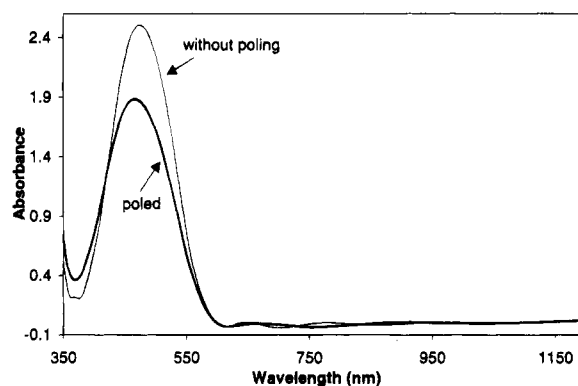
IR spectra. This demonstrates that the nitroazobenzene chromophores do not degrade during the thermal curing process. No isocyanurate function, whose characteristic absorption is at 1710 cm^{-1} (isocyanurate carbonyls), was observed in the spectra after the polymer was heated. This observation clearly indicates that the side reaction, trimerization of isocyanate to form isocyanurate, did not occur.

The UV–near-IR absorption spectra of the heterocyclic polymer, with and without poling, are shown in Figure 4. The spectra were obtained with films treated with the same heating profile described above and with or without the electric field applied. Using these procedures, the bleaching at ~480 nm caused by high temperature is eliminated from the data and the absorbance change solely resulted from the applied voltage. The absorption maxima with poling and without poling are 473 and 466 nm, respectively. The spectra exhibited a blue shift upon poling. The absorption peak is due to the intramolecular charge transfer band of the NLO chromophores. Since alignment of chromophore dipoles along the poling field direction, which is the incident light direction as well, will cause the peak absorbance to decrease, one can calculate the ordering

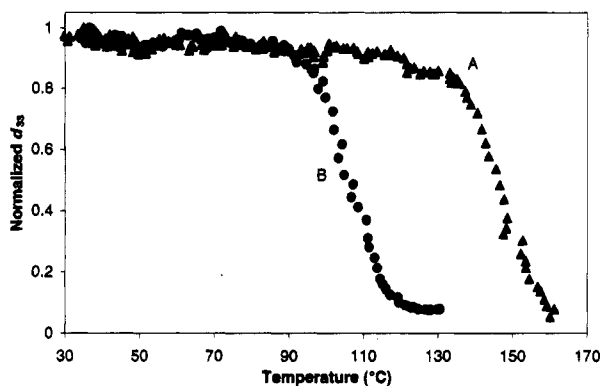(16) Uribe, M.; Hodd, K. A. *Polym. Prepr.* **1984**, *25*, 43.

Figure 5. Dynamic thermal stability of the heterocyclic polymer (curve A) and the cross-linked thermosetting polyurethane developed earlier by this group (curve B). Heating rate is 10 °C/min.

parameter of the poled films.[17] From the absorbance change, the ordering parameter was determined to be 0.26. The second-order NLO properties of the poled films were characterized by second harmonic generation (SHG) at 1064 nm fundamental wavelength, with a Y-cut quartz crystal ($d_{11} = 0.5$ pm/V) as the reference. A SHG d_{33} coefficient of 85 pm/V was obtained. This moderate value may be accounted for by the relatively low loading density of 24% of the NLO chromophore incorporated in the polymer and the relatively low β value of the NLO chromophore.

The dynamic thermal stability of the NLO activity of the heterocyclic polymer is shown in Figure 5 (curve A). The study of the real-time NLO stability of the polymer films as a function of temperature provides information on the 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 (i.e., 90% of the NLO signal remains after 1000 h) at temperatures approximately 30 °C below the temperature where the NLO activity starts to decrease.[18] Curve B was obtained from thermosetting polyurethane films treated according to procedures developed earlier.[15] This polyurethane is produced by cross-linking prepolymer 3 with triethanolamine. Because of its relatively high nonlinearity and excellent processibility, the thermosetting polyurethane is still being used for device fabrication years after its introduction. However, poor thermal stability is a serious problem with this material. The heterocyclic polymer described here (curve A) possesses the same processibility and higher stability. The rigidity of the heterocyclic ring is responsible for the improvement in thermal stability of the heterocyclic polymer.

In conclusion, we have prepared a new heterocyclic polymer with NLO chromophores covalently incorporated. The material exhibited excellent processibility, good thermal stability, and a moderate SHG signal. The synthesis scheme is desirable because it is easy to execute and can be extended to prepare other polymers with better NLO properties. We are currently synthesizing cross-linkable and higher β chromophores to incorporate into the system and produce materials with better stability and higher NLO activity.

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