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Processible and Thermally Stable Heterocyclic Polymers for Second-Order Nonlinear Optical Studies

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Following up on our preliminary communication, we present in this paper a novel approach to synthesize processible, cross-linkable, and thermally stable heterocyclic polymers (polyoxazolidones) with nonlinear optical properties. A cross-linkable NLO chromophore was synthesized and transformed into a prepolymer, which was easy to process and cross-link. After being efficiently poled and cured, the optical-quality films exhibited good nonlinearity and thermal stability. The stable, hardened lattice resulted from the formation of the heterocyclic ring. The details of synthesizing the cross-linked (trifunctional) and un-cross-linked (difunctional) heterocyclic polymers are presented. The effects of the processing conditions on the NLO properties are described. d_{33} coefficients of 77 and 85 pm/V at the 1.06 μm fundamental wavelength for the cross-linked and un-cross-linked polymers were obtained, respectively.

Introduction

Heterocyclic polymers are those polymers with cyclic components in which at least one of the ring members is a heteroatom. As heterocyclic polymers, including polyimides, are typically high-T_g polymers with excellent thermal stability, they are very good candidates for use in second-order nonlinear optical materials.[1−14]

Although high T_g is desired for second-order nonlinear optical materials to have stable NLO properties at high temperatures, it often results in unsatisfactory processibility and low poling efficiency. For example, inconvenient solvents, such as DMSO, and very high poling temperatures are required for the processing of many polyimide type NLO materials.[15,16] To overcome these difficulties, approaches were developed in this laboratory and elsewhere, in which processible polymers or oligomers were poled and thermally cured into cross-linked or heterocyclic polymers at reasonable temperatures. The aim of this work was to develop novel heterocyclic polymers with a good balance of second-order nonlinear susceptibility, nonlinear optical stability, and processibility. To obtain such NLO heterocyclic polymers, one may start with oligomers that are soluble in common organic solvents and can be processed into thin films. These oligomers should contain end-capped functional groups so that they can be thermally cured into heterocyclic polymers. However, one possible drawback is that during the curing process, as-yet unreacted oligomers and low molecular weight products may cross-link and form a spatially isolated network. In this sense, cross-linkable oligomers are preferable because they can be transformed more easily into polymers without the formation of low molecular weight products.

In a preliminary communication, we described an approach employing a NLO chromophore containing prepolymer to synthesize a novel thermally stable heterocyclic polymer.[17] In that approach, a cross-linking mechanism was not used, yet the un-cross-linked polymer still demonstrated better thermal stability than a cross-linked polyurethane with the same NLO chromophore. In this paper, we present the results of our extended work, including the effects of the processing conditions and additional cross-linking on the NLO properties of the heterocyclic polymers.

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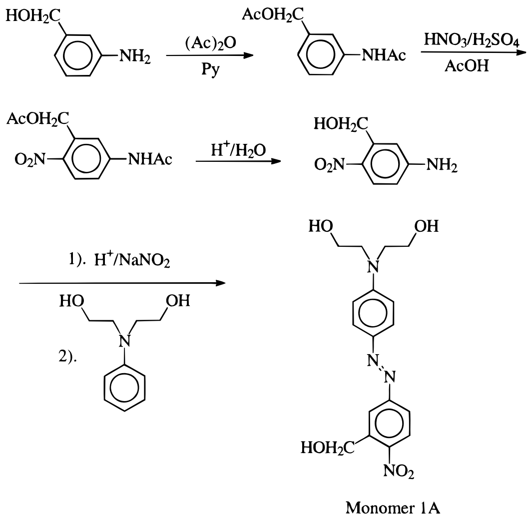

Figure 1. Synthesis scheme of monomer **1A**.

Experimental Section

General Materials and Methods. Fourier transform infrared spectra were obtained using a Perkin-Elmer 1760 FT-IR spectrophotometer. Thermal properties were measured by a Perkin-Elmer DSC-7 and a Perkin-Elmer TGA-7 system controlled by an IBM PS/2 computer, with a heating rate of 10 °C/min under an argon atmosphere. The polymerization solvents, dioxane and THF, and the catalyst, pyridine, were purchased from Aldrich and were further purified by distillation over sodium. They were stored in a drybox before use. 4,4′-Diisocyanato-3,3′-dimethoxydiphenyl was purchased from Pfaltz & Bauer and was purified by recrystallization from hexane or vacuum subliming prior to use. Other chemicals were purchased from various chemical companies and were used without further purification unless otherwise indicated.

Synthesis of Monomers. The intermediate materials and monomer 1A were synthesized according to the reaction schemes illustrated in Figure 1. Disperse Red 19 (monomer 1B) was synthesized according to literature procedures.[18]

3-Acetoxymethylacetanilide. In acetic anhydride (146.20 g) was dissolved 44.08 g (0.358 mol) of 3-aminobenzyl alcohol. The reaction was carried out by refluxing under nitrogen for 3 h. The reaction solution was poured onto 500 mL of crushed ice. The solid formed was filtered, washed with cold water twice, and dried in an oven at 60 °C overnight to obtain 55.60 g (75% yield) of white solid. ^{1}H NMR (CDCl$_3$) δ 7.57 (s, 1H), 7.54 (s, 1H), 7.47 (d, $J = 8.2$, 1H), 7.30 (t, $J = 7.7$, 1H), 7.09 (d, $J = 7.6$), 5.07 (s, 2H), 2.17 (s, 3H), 2.10 (s, 3H).

3-(Acetoxymethyl)-4-nitroacetanilide. To a solution of 225 mL of glacial acetic acid and 225 mL of concentrated sulfuric acid was added dropwise 63 mL of concentrated nitric acid (71%). After the resulting solution was cooled to 5 °C, 55.51 g (0.268 mol) of 3-(acetoxymethyl)acetanilide was added. The reaction solution was stirred at 10−15 °C for 3.5 h, and then it was poured into 600 g of ice and extracted with dichloromethane twice (total 350 mL). The organic solution was washed twice with brine and dried over sodium sulfate. Evaporation of the solvent gave a brown oil, which was recrystallized from 120 mL of toluene to yield 29.42 g (44%) of yellow crystals. ^{1}H NMR (CDCl$_3$) δ 8.15 (d, $J = 9.0$, 1H), 7.90 (s, br, 1H), 7.81 (d, $J = 2.3$, 1H), 7.63 (dd, $J = 9.0$, $J = 2.3$, 1H), 5.53 (s, 2H), 2.24 (s, 3H), 2.20 (s, 3H).

3-(Hydroxymethyl)-4-nitroaniline. To a solution of 38 mL of hydrochloric acid (37%) and 180 mL of water was added 29.36 g of 3-(acetoxymethyl)-4-nitroacetanilide. The solution was refluxed for 1.5 h under nitrogen and cooled to room temperature; the resulting solution was neutralized with 15% NaOH solution to pH = 7. The precipitate was collected by filtration, washed with 15 mL of cold water, and dried in an oven at 50 °C overnight; 18.42 g (93% yield) of yellow crystals was obtained. ^{1}H NMR (acetone-d_6) δ 7.98 (d, $J = 9.0$, 1H), 7.14 (m, 1H), 6.62 (dd, $J = 9.0$, $J = 2.5$, 1H), 6.60 (s, br, 2H), 4.94 (d, $J = 5.1$, 2H), 4.42 (t, $J = 5.5$, 1H). ^{13}C NMR (DMSO-d_6) δ 155.1, 143.4, 133.7, 128.3, 110.8, 110.4, 60.9. Anal. Calcd for $C_7H_8N_2O_3$: C, 49.99; H, 4.78; N, 16.66. Found: C, 50.00; H, 4.77; N, 16.60.

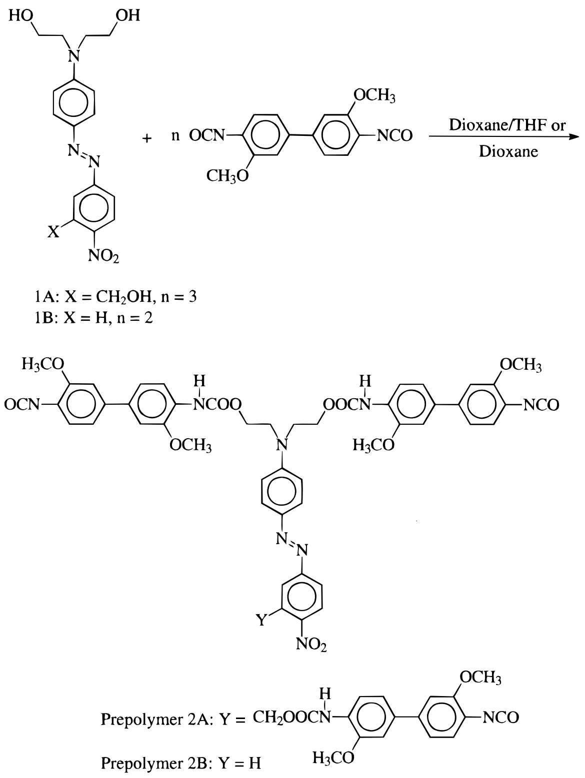

Figure 2. Synthesis schemes of the prepolymer **2A** and **2B**.

Monomer 1A. To an ice-cooled solution containing 3-(hydroxymethyl)-4-nitroaniline (0.25 g, 1.5 mmol) and 3% hydrochloride solution (15 mL) was added dropwise a sodium nitrite solution (0.14 g, 2 mmol in 2 mL of water). 15 min after adding the last drop of the sodium nitrite solution, *N*,*N*-bis(2-hydroxyethyl)aniline (0.27 g, 1.5 mmol) in 7% HCl solution was added. The resulting mixture was stirred below 5 °C for another 2 h and then neutralized with 10% NaOH solution. A deep red precipitate was collected, washed three times with ethanol/water (1:1), and then dried to obtain 0.40 g of red solid. ^{1}H NMR (DMSO-d_6) δ 8.22 (d, $J = 8.7$, 1H), 8.18 (d, $J = 1.8$, 1H), 7.85−7.79 (m, 3H), 6.90 (d, $J = 9.2$, 2H), 5.69 (t, $J = 5.1$, 1H), 4.89 (m, 2H), 4.72 (s, br, 2H), 3.60 (m, br, 8H). ^{13}C NMR (DMSO-d_6) δ 155.1, 152.2, 145.6, 142.6, 140.7, 126.2, 125.9, 120.5, 111.6, 60.2, 58.2, 53.3.

Synthesis of Prepolymers. The prepolymers were prepared according to the reaction scheme shown in Figure 2.

*Prepolymer **2A**:* To a round-bottom flask containing dioxane (14.0 mL) and THF (6.0 mL) was added monomer **4** (0.3604 g, 1.00 mmol) and 4,4′-diisocyanato-3,3′-dimethoxydiphenyl (**2**, 0.9176 g, 3.10 mmol). Two drops of pyridine was added as a catalyst. The resulting mixture was heated to reflux for 3 h under an argon atmosphere. The solution was cooled to room temperature and then filtered through a 0.2 μm Teflon filter. The solvent was pumped out by vacuum, and the obtained red solid prepolymer (1.125 g, 88%) was then stored in a drybox.

*Prepolymer **2B**:* 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. No catalyst was added to avoid cross-linking. The resulting mixture was heated to reflux for 2 h under an argon atmosphere. 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 the drybox.

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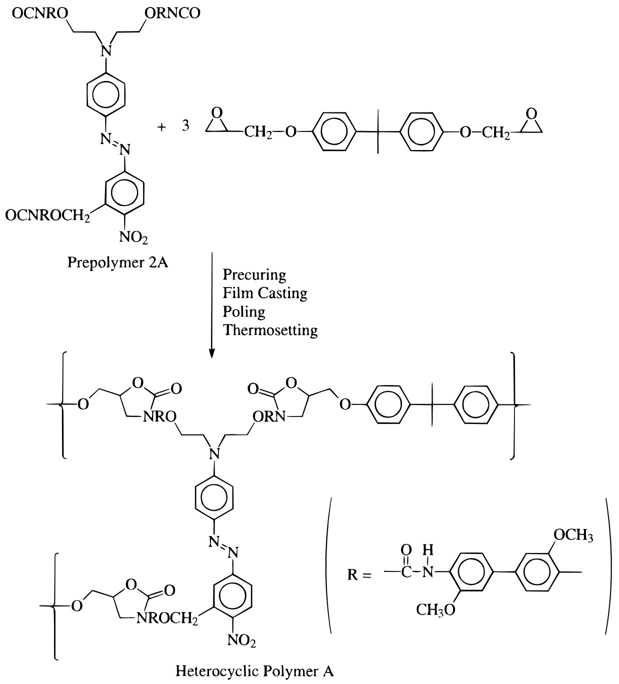

Figure 3. Synthesis scheme of preparing the cross-linked heterocyclic polymer.

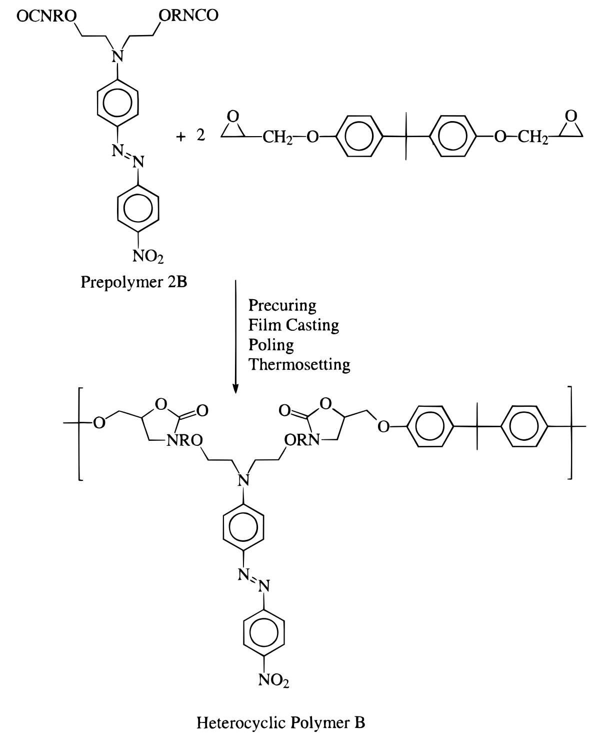

Figure 4. Synthesis scheme of preparing the un-cross-linked heterocyclic polymer.

Preparation of NLO Films and Poling/Curing. The heterocyclic polymerization schemes to prepare the cross-linked polyoxazolidone (polymer A) and un-cross-linked linear poly-2-oxazolidone (polymer B) are shown in Figures 3 and 4, respectively. Bisphenol A diglycidyl ether (BADGE) (0.8510 g, 2.500 mmol) was dissolved in 25.00 mL of dioxane to form a 0.100 mM solution for use in preparing the prepolymer films.

Cross-Linkable Prepolymer Films. Prepolymer **2A** (0.8744 g, 0.07 mmol) was dissolved in a solution of 0.30 mL of THF and 1.05 mL of BADGE/dioxane (0.105 mmol of BADGE). The resulting solution was filtered through a 0.2 μm Teflon filter and then it was spun-cast onto transparent glass slides coated with an ITO conductive layer as a poling electrode. Occasionally, precuring was required. The films obtained were dried overnight in a vacuum at room temperature.

Un-Cross-Linkable Prepolymer Films. Prepolymer **2B** (0.092 29 g, 0.1 mmol) was dissolved in a 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 it was spun-cast onto transparent glass slides coated with an ITO conductive layer as a poling electrode. Before spinning, the filtered solution was heated to 110 °C on a hot plate for several minutes to precure the prepolymer. The films obtained were dried overnight in a vacuum at room temperature.

For both prepolymers, optical-quality thin films were routinely obtained. 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 freeze in the poling-induced order. The poling voltages and temperatures, which affect both the poling efficiency and polymerization, were selected based on FT-IR studies and poling tests. This enabled optimal poling efficiency and complete polymerization while preserving the film quality. Multistep poling profiles were used to accommodate the curing reaction which starts at low temperature. Higher temperatures were needed to complete the polymerization which improves the thermal stability.

Optical Measurements. The absorption spectra of the polymer films, before and after corona poling, were measured with a Cary 2415 spectrophotometer operating in the wavelength range 350–1200 nm. The films were placed perpendicular to the incident beam in the spectrophotometer sample compartment. An uncoated ITO glass slide was used to correct the measurement background. Second harmonic generation (SHG) was employed to measure the second-order optical nonlinearities of the polymer films. The dynamic NLO stability of the polymer films was measured with a heating rate of 10 °C/min. This provides a measure of the real-time NLO performance as a function of temperature.[19]

Results and Discussion

Synthesis and Characterization of Polymers. Two nitroazobenzene chromophores, one with two hydroxyl groups and the other with three hydroxyl groups, were chosen to synthesize a linear chain and a cross-linked heterocyclic polymer, respectively. They serve as the samples to study and compare such properties as poling efficiency and thermal stability. 4,4′-Diisocyanato-3,3′-dimethoxydiphenyl was chosen as part of the polymer backbone because it can increase the rigidity of the polymer chain. No catalyst was used in preparing prepolymer 2B to avoid possible cross-linking reactions. A trace amount of pyridine was used as a catalyst in preparing prepolymer **2A** because the chromophore does not easily dissolve in the solvent, which makes the reaction more difficult to occur. Pyridine was chosen to catalyze the reaction because it is a mild amine and can be removed easily from the prepolymer. An extra 3–5% of 4,4′-diisocyanato-3,3′-dimethoxydiphenyl was added to facilitate the formation of the prepolymers and to react with any moisture present. The remaining 4,4′-diisocyanato-3,3′-dimethoxydiphenyl can be removed by filtration because it does not dissolve in the solvent at room temperature. Filtration through a 0.2 μm filter not only purified the prepolymer but also made the prepolymer easier to dissolve when preparing polymer films.

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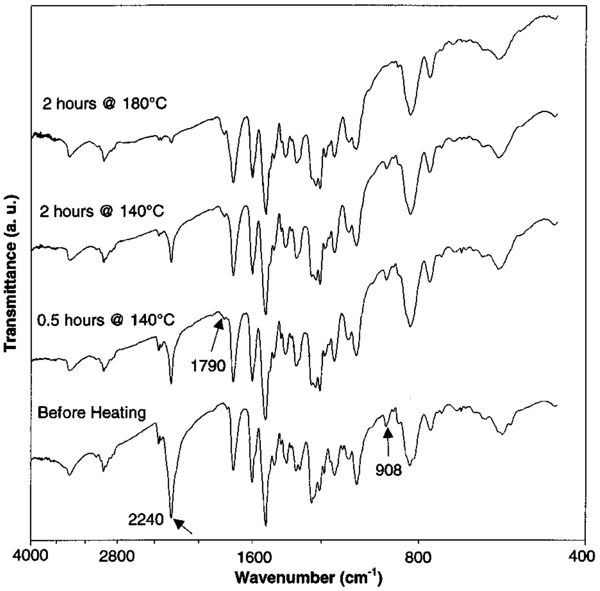

Figure 5. FT-IR spectra of the cross-linked heterocyclic polymer at different polymerization stages. The arrows at 2240, 1790, and 908 cm^{-1} indicate the disappearing isocyanate group, the emerging oxazolidone function, and the disappearing epoxy function, respectively.

The isocyanate group in the prepolymer reacts with the epoxy group to form oxazolidone upon heating.[20] This is demonstrated by the FT-IR spectra of the prepolymer **2A** with diepoxy heated at different temperatures for different periods of time as shown in Figure 5. When the prepolymer with a stoichiometrically equal amount of diepoxy added was heated at 140 °C, the peak at 2240 cm^{-1} associated with the isocyanate and the peak at 908 cm^{-1} associated with the epoxy decreased, while the peak at 1790 cm^{-1} associated with the oxazolidone appeared. After the polymer was further heated at 180 °C for 2 h, the peaks at 2240 and 908 cm^{-1} almost completely disappeared, indicating that the polymerization was nearly complete. The FT-IR spectra also provided information on the effect of temperature on polymerization. It was found that though polymerization occurs at 120 °C, it requires temperature up to 180 °C for several hours to go to completion. 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 polymers were heated. This observation clearly indicates that the side reaction (trimerization of the isocyanate to form isocyanurate) did not occur.

The polymerization reaction was also characterized by DSC analyses. Both prepolymers with BADGE exhibited a wide endothermic change in the DSC thermograms. As shown in Figure 6 for prepolymer 2A, the endotherm started at ca. 100 °C and completed at ca. 170 °C. The cured polymer does not show such a change. TGA analyses of the prepolymer and cured polymers are shown in Figure 7. As might be expected, the cured cross-linked polymer is more stable than cured un-cross-linked polymer, and the prepolymer is the least stable. The cured polymers were very tough and were completely insoluble in the reaction media dioxane or dioxane/THF. This indicates tough, stable polymers were formed.

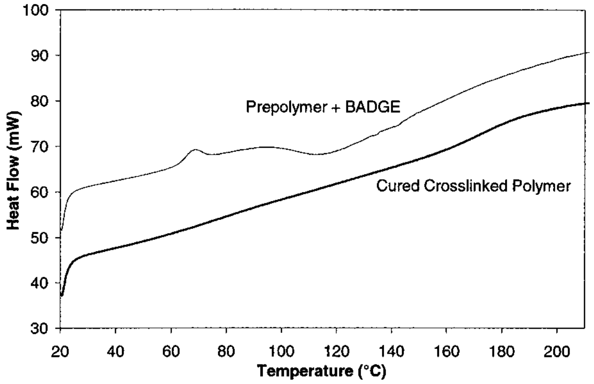

Figure 6. DSC traces of the prepolymer **2A** with a stoichiometrically equal amount of BADGE and the cured cross-linked polymer.

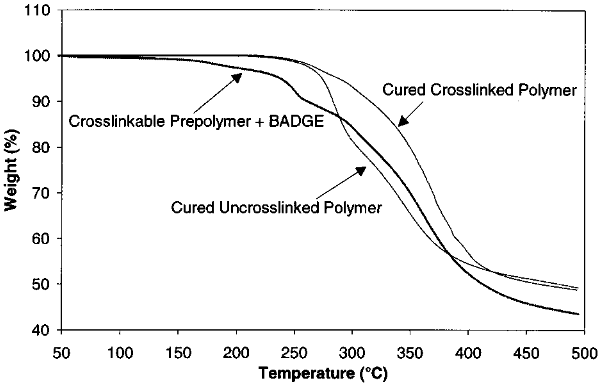

Figure 7. TGA traces of the prepolymer **2A** with BADGE, cured cross-linked polymer A, and cured un-cross-linked polymer B.

NLO Properties. From the FT-IR and DSC studies, it can be inferred that the polymerization requires a longer time to complete at low temperature than at high temperature. It would be desirable if the films could be poled and cured at high temperature, such that a shorter process time would be needed. Experiments showed, however, that curing and poling at a high temperature (180 °C) would damage the films, especially at the beginning when most of the prepolymers have not reacted. A low temperature (140 °C), therefore, was used to cure and pole the films. To avoid damage to the films by high voltage, the films were heated to 170–180 °C for 1–5 min to precure the polymer before voltage was applied.

Since the chromophore in the cross-linked polymer is attached at three sites, shorter precuring time was used to control the cross-linking density, otherwise the polymer would be difficult to pole. To pole the cross-linked polymer films, they were first heated to 170 °C for 1 min. They were then cooled to 140 °C, and a 6 kV corona voltage was applied. Application of a 9 kV voltage occurred 5 min later. The delayed use of the maximum corona voltage allows sufficient film hardening to avoid surface damage. The 140 °C poling continued for 20 h. For the un-cross-linked polymer, a longer precuring step is necessary. In a typical poling profile of this polymer, the films were heated to 180 °C for 5 min and then cooled to 140 °C for 5 h before a corona

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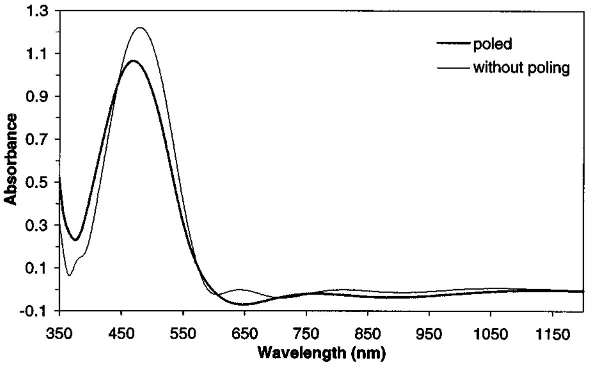

Figure 8. UV−near-IR absorbance of the cross-linked polymer with and without poling. The negative absorbance values with respect to an uncoated reference substrate are due to Fabry−Perot interference effects in the film.

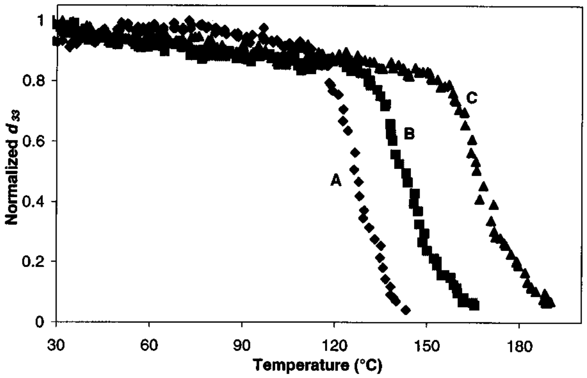

Figure 9. Dynamic thermal stability of the cross-linked heterocyclic polymer poled at different stages are shown. (A) poled for 1 h. (B) 10 h. (C) 20 h.

voltage of 6 kV was applied. 1.5 h later, 9 kV was applied, and poling was continued for another 13.5 h.

The UV−near-IR absorbance spectra of the cross-linked polymer film with and without poling are shown in Figure 8. Both films tested underwent the previously mentioned heating profile with or without an applied corona voltage, as indicated. Comparison of the two spectra enables the elimination of any bleaching effects caused by temperature alone. The remaining absorbance change, resulting solely from the applied corona voltage, is due to the intramolecular transfer band of the NLO chromophores. Since alignment of the chromophore dipoles along the poling field direction causes the absorbance peak to decrease, one can calculate the ordering parameter of the poled film.[21]

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. Efficient poling resulted in repeatable d_{33} values of 77 and 85 pm/V for the cross-linked and un-cross-linked polymers, respectively. Figure 9 shows the dynamic stability for cross-linked films that were poled for 1 h (curve A), 10 h (curve B), and 20 h (curve C). This illustrates the dramatic increase in thermal stability that results from poling times of up to 20 h. It also verifies the long times required to fully cure the cross-linked polymer.

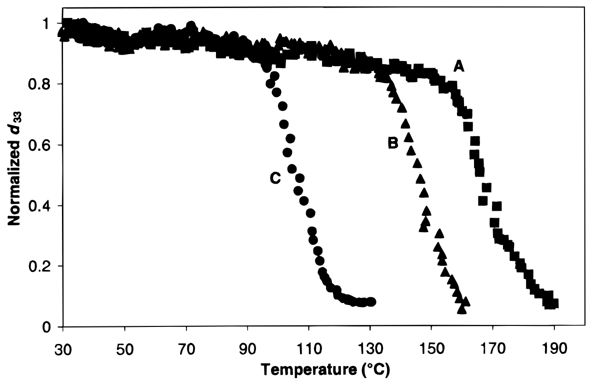

Figure 10. Dynamic thermal stability of the cross-linked heterocyclic polymer (curve A), un-cross-linked heterocyclic polymer (curve B), and the cross-linked thermosetting polyurethane developed earlier by Dalton et al.[17] (curve C).

Table 1. Loading Density, Dynamic Stability, and SHG Signal

sample	loading (%)	stability (°C)	d_{33} (pm/V)
cross-linked heterocyclic polymer	14	155	77
un-cross-linked heterocyclic polymer	24	135	85
cross-linked polyurethane	32	95	120

The NLO dynamic thermal stabilities of the cross-linked and un-cross-linked heterocyclic polymers are shown in Figure 10 (curves A and B). Curve C was obtained from thermosetting polyurethane films treated according to procedures developed earlier.[18] This polyurethane is produced by cross-linking prepolymer **2B** 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, low thermal stability is a serious problem with this material. The heterocyclic polymers described here possess the same processibility but with a higher thermal stability. The rigidity of the heterocyclic ring is responsible for the dramatic improvement in the stability of the heterocyclic polymer. Cross-linking further improves the thermal stability. The relatively low loading densities of the heterocyclic polymers are responsible for their moderate nonlinearities as shown in Table 1.

Conclusion

In conclusion, we have prepared novel heterocyclic polymers where NLO chromophores were covalently incorporated into the system. The materials exhibited excellent processibility, good thermal stability, and moderate SHG signal. A relatively low loading density, however, is a drawback of this system. Nevertheless, the synthesis scheme is desirable because of its simplicity and potential for incorporating chromophores with greater nonlinearities.

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