Isocyanate Cross-Linked Polymers for Nonlinear Optics. 1. Polymers Derived from 3-Amino-5-[4'-(N-ethyl-N-(2''-hydroxyethyl)amino)benzylidene]-rhodanine

Cecil V. Francis,* Kenneth M. White, Gary T. Boyd, Robert S. Moshrefzadeh, Sarat K. Mohapatra, Marc D. Radcliffe, John E. Trend, and Robert C. Williams

3M Corporate Research Laboratory, Bldg. 201-2E-08, St. Paul, Minnesota 55144-1000

Novel difunctional nonlinear optical molecules have been synthesized. These molecules, having functionalities that differ in their reactivities at each end, have been converted to thermally cross-linked polyurea–polyurethane. The stability of the nonlinear optical response for the poled cross-linked polymer at 100 °C has been studied by second harmonic generation and UV–vis spectroscopy. The results suggest that decay of the nonlinear optical response was due to chromophore degradation rather than relaxation of the polar orientation. Single-mode optical channel wave guides displayed propagation loss less than 1 dB/cm at 1330 nm. Channel waveguide intensity modulators displayed an electrooptic coefficient of 3.3 pm/V.

Introduction

Many researchers have focused on organic polymeric materials for nonlinear optical (NLO) applications. Initially, guest–host systems, in which the NLO-active molecule (NLO-phore) was dissolved in a host polymer and poled in an electric field after film casting, were investigated.[1] Despite extensive processing, only modest stability of the polar orientation of the NLO-phore could be achieved even at room temperature.[2–5]

In an effort to improve the alignment stability of the dipoles and to increase the concentration of the NLO-phores in the polymer, side-chain polymers were investigated.[6] These systems showed improved compatibility between the polymer and NLO-phore, resulting in the attainment of higher concentrations of the NLO-phores in the polymer compared to most guest–host mixtures. The alignment stability of the dipoles improved dramatically, depending on the glass transition temperature (T_g) of the polymer, but the relaxation time of the alignment above room temperature remained impracticably short.

To address the inhibition of dipole relaxation at elevated temperatures, cross-linked polymers were investigated. Two general approaches have been taken: cross-linking around a pendant NLO-phore to restrict the free volume and cross-linking through the NLO-phore. Several reports have appeared on the former case, and improvements have been reported in the maintenance of dipole orientation at elevated temperatures.[7–10] In the latter case only a few

reports have appeared in the open literature. Amine-cured epoxide systems have been reported to show no sign of dipole relaxation at 85 °C.[11,12] Mandal et. al. have also reported on the use of 2+2 photodimerization of cinnamoyl groups.[13] In this instance, although improved dipole stability at elevated temperatures was reported, the concentration of the NLO moiety in the system was low.

We have investigated cross-linking through the NLO-phore with a different perspective from the above-described systems. We have synthesized bifunctional NLO-phores containing differentially reactive groups at each end. This difference in reactivity was designed to allow a stepwise reaction of this molecule to form oligomers which could be processed into optical quality films. The reaction conditions are subsequently changed while applying the electric field to allow for the reaction of the second functionality once the NLO-phore has been poled, thus yielding a cross-linked matrix with a multifunctional comonomer. The rationale here is that the NLO-phore, chemically bound at both ends in a cross-linked network, will be severely restricted in rotation. This should result in significant reduction in relaxation of the polar alignment even at elevated temperatures.

Experimental Section

Synthesis. 2-Thioxo-4-thiazolidinone (rhodanine), 3-aminorhodanine, 3-methylrhodanine, 2-(ethylamino)ethanol, and fluorobenzaldehyde were obtained from Aldrich Chem. Co. and used without further purification. Tolonate HDT, the triisocyanate isocyanurate made from 1,6-hexamethylene diisocyanate,

(1) Singer, K. D.; Sohn, J. E.; Lalama, S. L. *Appl. Phys. Lett.* 1986, *49*, 248.

(2) Meredith, G. R.; Van Dusen, J.; Williams, D. J. *Macromolecules* 1982, *15*, 1385.

(3) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* 1988, *21*, 526; 1990, *23*, 3640; 1990, *23*, 3648.

(4) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Polym. Commun.* 1989, *30*, 40.

(5) Boyd, G. T.; Francis, C. V.; Trend, J. E.; Ender, D. A. *J. Opt. Soc. B* 1991, *8*, 887.

(6) See for example *Nonlinear Optical Properties of Organic Materials III*; Khanarian, G., Ed. *Proc. SPIE* 1990, 1337; *Polym. Prepr.* 1991, *32* (2); Culbertson, W. M., Ed.

(7) Yu, L.; Chan, W.; Dikshit, S.; Bao, Z.; Shi, Y.; Steier, W. H. *Appl. Phys. Lett.* 1992, *60*, 1655.

(8) Shi, Y.; Steier, W. H.; Chen, M.; Yu, L.; Dalton, L. R. *Appl. Phys. Lett.* 1992, *60*, 2577.

(9) Tatsuura, S.; Sotoyama, W.; Yoshimura, T. *Appl. Phys. Lett.* 1992, *60*, 1158.

(10) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* 1989, *1*, 167.

(11) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* 1989, *66*, 3241.

(12) Jungbauer, D.; Teraoka, I.; Yoon, D. Y.; Willson, C. G.; Swallen, J. D. *Appl. Phys. Lett.* 1990, *56*, 2610.

(13) Mandal, B. K.; Kumar, J.; Huang, J. C.; Tripathy, S. K. *Makromol. Chem., Rapid Commun.* 1991, *12*, 63.

Isocyanate Cross-Linked Polymers for Nonlinear Optics

Chem. Mater., Vol. 5, No. 4, 1993 507

was obtained from Rhone-Poulenc and was also used without further purification. NMR spectra were taken on a 400-MHz Varian spectrometer. Melting points are uncorrected.

Synthesis of 4-(N-ethyl-N-(2'-hydroxyethyl)amino)-benzaldehyde: A general procedure for the preparation of amino-substituted benzaldehydes was adapted from Tournilhac.[14] A mixture of 54.3 g (0.610 mol) of 2-(ethylamino)ethanol, 50 g (0.400 mol) of 4-fluorobenzaldehyde, 50 g (0.362 mol) of anhydrous potassium carbonate, and 50 mL of dimethyl sulfoxide was heated to 120 °C for 4 days under nitrogen atmosphere. After cooling to room temperature, the reaction was diluted with 1 L of water. The aqueous solution was extracted with dichloromethane; the organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator under reduced pressure and the product dried under high vacuum overnight to afford 75.3 g (96%) of 4-[N-ethyl-N'-(2-hydroxyethyl)amino]benzaldehyde: ^{1}H NMR (CDCl$_3$) δ 1.2 (t, 3, CH$_3$), 3.5 (m, 4, NCH$_2$), 3.8 (t, 2, OCH$_2$), 6.7 (d, 2, ArH), 7.7 (d, 2, ArH(, 9.7 (s, 1, CHO).

The NLO-phores were all synthesized from an aminobenzaldehyde derivative by modifying the method of Campbell and McKail.[15] A representative synthesis is shown.

Synthesis of 3-amino-5-[4'-(N-ethyl-N-(2''-hydroxyethyl)amino)benzylidene]rhodanine (I): 3-Aminorhodanine (3.07 g, 0.0207 mol) was refluxed in ethanol (30 mL) to effect dissolution. 4-(N-Ethyl-N-(2'-hydroxyethyl)aminobenzaldehyde (4.00 g, 0.0207 mol) dissolved in ethanol (10 mL) was added, and the resultant mixture was refluxed for 2 h before it was cooled to room temperature. The red crystals that formed were filtered to yield 6.5 g (97%) product, mp = 140–141 °C: ^{1}H NMR (DMSO-d_6) δ 1.12 (t, 3, CH$_3$), 3.50 (m, 4, NCH$_2$), 3.57 (t, 2 OCH$_2$), 5.95 (s, 2 H, NH$_2$), 6.85 (d, 2 H, ArH), 7.46 (d, 2 H, ArH), 7.70 (s, 1 H, CH). $λ_{max}$ 471 nm (ethanol).

Polymer Preparation/Processing. Synthesis and processing of a cross-linked polymer: 3-amino-5-[4'-(N-ethyl-N-(2''-hydroxyethyl)amino)benzylidene]rhodanine was dissolved in freshly dried pyridine (distilled from CaH$_2$). To this solution was added 10% equivalent excess Tolonate HDT, and the resulting solution was warmed to 50 °C for 30 min. This solution was filtered through a 0.2-μm filter, and then films were formed by spin coating under clean conditions. The films were dried at 75 °C for 1 h and could be cross-linked upon further heating above 75 °C.

Index of Refraction. The index of refraction of the polymer was measured using a grating coupling technique.[16] A photoresist grating with a period of 1.5 μm was patterned on a thermally oxidized silicon wafer using laser interference at 442 nm. Next, the grating pattern was etched into the SiO$_2$ layer using reactive ion etching (RIE) with carbon tetrafluoride. Subsequently, the substrate was thoroughly cleaned, dried, and coated with a 2–3-μm-thick layer of polymer.

Incident laser radiation was coupled to various modes of such a polymer slab wave guide in the grating at well-defined incident angles. These angles were measured at a wavelength of 1.3 μm from which the film thickness and index were calculated. The index was measured both after soft-bake (75 °C for 1 h) and hard-bake (150 °C for 4 h, sufficient to cross-link the polymer).

Poling and Stability Measurements. The poling process and $χ^{(2)}$ decay were monitored using second harmonic generation (SHG) at a fundamental wavelength of 1.58 μm. The incident laser pulses were generated using the third Stokes output from a hydrogen Raman cell pumped by frequency doubled 1.06-μm pulses from a Nd:YAG laser (Quanta-Ray DCR-3). The pulse repetition rate, pulse width, and peak energy per pulse were 10 Hz, 8 ns, and 0.3 mJ, respectively. Polymer films were prepared, as described above, by spin-coating a pyridine solution of the polymer onto coplanar chromium electrodes on fused silica microscope slides. The electrodes were 1 cm wide, separated by a 150-μm gap. Dried, spun films were typically 2 μm thick. The sample was then mounted onto a copper heating stage equipped with high-voltage electrodes and placed in a chamber purged with flowing dry nitrogen. The laser pulses entering the chamber
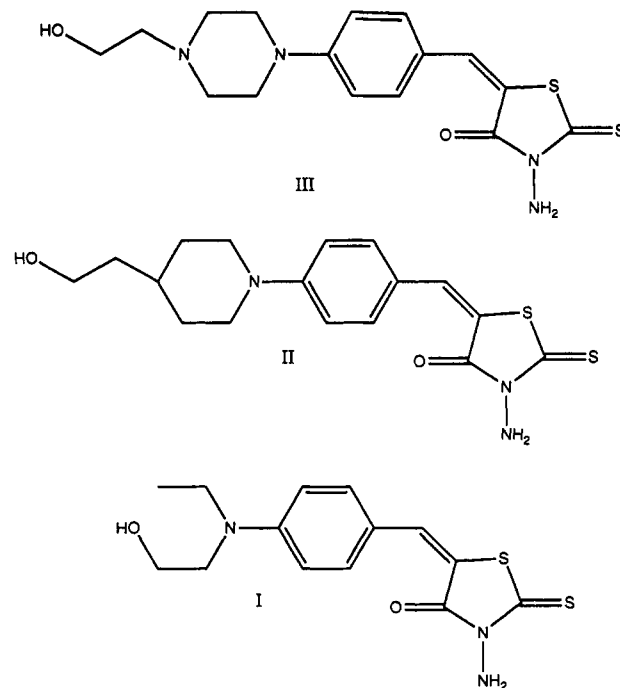

Figure 1. Bifunctional NLO-phores synthesized.

were focused through the electrode gap using a cylindrical lens. The exiting SHG signal was imaged through color filters into a monochromator tuned to 790 nm. A Hamatsu R928 photomultiplier tube was used to detect the second harmonic pulses which were processed using a boxcar averager (EG&G 4402).

A typical poling cycle for the polymer film started with the application of 1 kV across the electrode gap at room temperature, maintaining this field at 75 °C for 1 h and 150 °C for 16 h to ensure complete cross-linking. Current levels were typically on the order of 0.1 nA. The second harmonic signal was observed to rise slightly at room temperature with the application of the field, indicating low rotational mobility at this temperature. A rapid rise in signal ensued during subsequent heating at threshold temperatures which varied with the degree of drying time. At 150 °C, the SHG signal was observed to slowly decay with the field applied, suggesting NLO-phore degradation or local field changes. Since current levels were observed to decrease only slightly during the curing process, local field changes were assumed to be small. After the poling process, the samples were cooled to room temperature at a rate of approximately 5 °C/min, and a base-line $χ^{(2)}$ measurement was made relative to a quartz crystal reference. The films were then placed in a vacuum oven maintained at 100 °C and continuously flushed with dry nitrogen. Stability measurements were carried out over a 6-month period by periodically removing the samples into the ambient air, placing them in the original poling stage and maximizing the SHG signal by aligning the electrode gap with the incident beam. A quartz reference measurement was taken immediately thereafter, and the sample was returned to the nitrogen purged oven.

Poling of spin-coated polymer films at high fields (1 MV/cm) was performed on 2.2-μm-thick samples coated onto glass substrates having indium tin oxide (ITO) electrodes. A 90-Å layer of gold, vapor deposited on the polymer, served as the top electrode. The samples were poled in an oven through which a laser beam was passed for monitoring SHG in a manner similar to that described above. The films were cured in ambient atmosphere at 135 °C with the field applied for a given amount of time and then cooled to room temperature (~4 °C/min) before removing the field. The films were subsequently heated to 100 °C in ambient atmosphere and decay of $χ^{(2)}$ was monitored using SHG. UV–visible spectra used to observe changes in the films were obtained with a Shimadzu UV 3101 spectrophotometer.

Results and Discussion

Film Formation and Curing. Bifunctional NLO-phores shown in Figure 1 were synthesized, and their

(14) Tournilhac, F.; Nicoud, J. F.; Simon, J.; Weber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1987**, *2*, 55.

(15) Campbell, N.; McKail, J. E. *J. Chem. Soc.* **1948**, 1251.

(16) Moshrefzadeh, R. S.; Mai, X.; Seaton, C. T. *Appl. Opt.* **1987**, *13*, 2501.

solubility in pyridine was examined. 3-Amino-5-[4'-(*N*-ethyl-*N*-(2''-hydroxyethyl)amino)benzylidene]-rhodanine (I) had the greatest solubility, making it the dye of choice for polymer incorporation. All the dyes synthesized for polymer synthesis are bifunctional with two groups of differing reactivities.

Reaction of amines and alcohols with isocyanates to form ureas and urethanes, respectively, are well-known and have been studied in great detail.[17] The differential reactivities of amines and alcohols are being exploited by the functionalities incorporated in these NLO-phores with the intent that the amine reacts first to enable coating of the film and that the alcohol reacts at elevated temperatures during poling to cross-link the film.

To determine whether a stepwise reaction does in fact occur in this system, comparative infrared spectroscopy (IR) was used to study several derivatives of I. Bands corresponding to the amine and alcohol functionalities were identified and monitored for disappearance as the urea- and urethane-forming reactions progressed. For the amine reaction, the disappearance of a broad and intense band at 940 cm^{-1} assigned to the NH$_2$ wag in I was monitored. This band was absent in IR spectra of films measured immediately after spin coating, indicating that the amine reaction nearly reaches completion during the 50 °C processing prior to spin coating. Quantitative monitoring of the isocyanate band at 2270 cm^{-1} at this stage also revealed that just under 1 equiv of the Tolonate HDT had been consumed. Since 1 equiv is needed to react all of the amine, this implied that, as desired, little urethane had formed. Although the amine functionality in these NLO dyes is predicted to be less basic than in aliphatic or simple aromatic amines, additional IR studies showed that reaction with the isocyanate proceeds readily at room temperature.

In the cross-linking step, the reaction of the alcohol with the isocyanate was followed by means of the band at 1050 cm^{-1} associated with the primary alcohol. In the reaction of the methyl rhodanine derivative of I with Tolonate HDT at 100 °C for 16 h, this band disappeared almost completely after the consumption of 1 equiv of the isocyanate, as monitored by the 2270-cm^{-1} band. When curing I at elevated temperatures (>75 °C), similar diminution of the alcohol band is observed, although it never completely vanishes, even upon disappearance of the isocyanate band. It is possible that not all of the alcohol in the film reacts with the isocyanate. This could be due to lack of mobility or proximity of the appropriate functionalities in the cross-linked film as the reaction nears completion. In this case, the isocyanate is likely consumed by reaction with water or by production of biurets and allophanates.[17]

Since the curing step must occur simultaneously with poling of the polymer film, cure rate as a function of temperature is another vital parameter for processing the electrooptic film. Such a study was carried out by monitoring the 2270-cm^{-1} band in the IR spectrum to determine the amount of unreacted isocyanate at any given time. The results are shown in Figure 2 for films cured at 75, 100, 125, and 150 °C after having been dried for 4 h at 75 °C. The data show that 35% of the isocyanate groups are still unreacted after drying, indicating that a majority of the dye is still free to be poled prior to cross-linking. Only the 150 °C cure exhibited complete reaction of the isocyanate groups within the 1-day period shown.
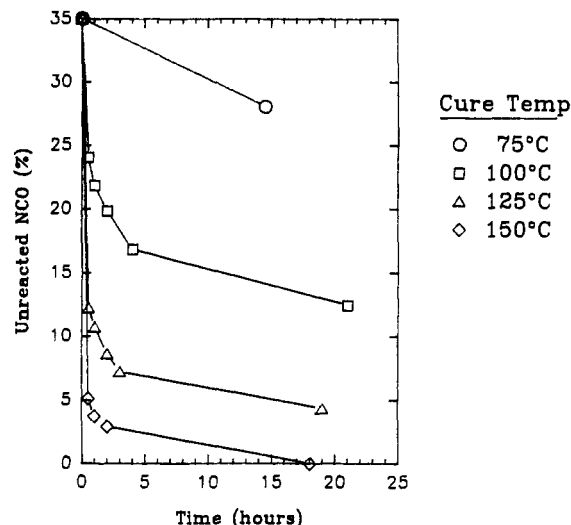

Figure 2. Curing study of the polymer film derived from compound I as a function of time at various curing temperatures. The consumption of isocyanate was monitored using infrared spectroscopy.
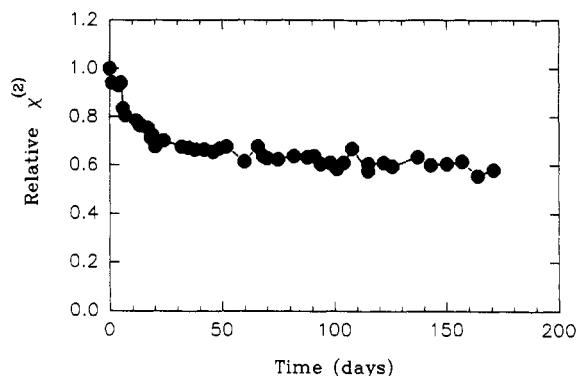

Figure 3. Decay of $\chi^{(2)}$, as determined from SHG measurements, for the poled and cross-linked polymer film derived from compound I. The sample was maintained at 100 °C.

Residual isocyanate was detected in the film cured at 125 °C, even after an additional 2 days of curing.

Poling Stability. The long-term stability of $\chi^{(2)}$ or the electrooptic (E-O) coefficient (r) for poled polymers is of critical importance for all device applications. The most useful measurements of stability are made at or above the highest operating temperature projected for E-O applications. Mechanisms for $\chi^{(2)}$ decay with time include randomization of the orientation of the poled dipoles and degradation of the NLO-phores. Since degradation of the NLO-phores typically causes a significant drop in the molar absorptivity as well, a simple means to isolate these two causes for decay is to simultaneously measure $\chi^{(2)}$ and the absorption spectrum. The decrease in $\chi^{(2)}$ can then be normalized to the change in absorptivity to discern the orientational decay component. Other workers[18,19] have used dichroic and birefringence measurements to determine the orientational decay of other polymeric systems.

The results of the SHG stability measurements on several samples are shown in Figure 3. The $\chi^{(2)}$ decay, obtained by taking the square root of the SHG signal relative to the initial baseline measurement, shows a significant amount of scatter which we attribute to

(17) Saunders, K. J.; Frisch, K. C. *Polyurethanes, Chemistry and Technology*; Wiley: New York, 1967.

(18) Page, R. H.; Jurich, M. C.; Reck, B.; Sen, A.; Tweig, R. J.; Swalen, J. D.; Bjorklund, G. C.; Willson, C. G. *J. Opt. Soc. Am. B* **1990**, *7*, 1239.
(19) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733.

Isocyanate Cross-Linked Polymers for Nonlinear Optics

Chem. Mater., Vol. 5, No. 4, 1993 509

alignment errors of the incident beam and the electrode gap. A relatively rapid initial drop in $\chi^{(2)}$ is observed, followed by a slower decay. Such multiple time constant decays have been observed by several investigators[1,3,4,10] and attributed to a broad distribution of local decay times in a glassy matrix.[1,11,12]

High-field poling results show that a film poled and cured for 16 h at 1 MV/cm exhibits the same decay in $\chi^{(2)}$ as one poled at low field (67 kV/cm). In addition, polymer films poled and cured for only 1 or 2 h displayed essentially the same decay rate. Only when the cure time dropped below 1 h was a faster decay in $\chi^{(2)}$ observed.

During the course of the poling experiments, it was found that the polymer films bleached noticeably as a result of heating. To determine the relationship between this bleaching process and $\chi^{(2)}$ decay in the polymer films, two experiments comparing UV–vis spectroscopic measurements with SHG data were performed. In the first experiment, two identical sets of guest–host films of I in PMMA (15% w/w) were prepared. Each set contained two identical films, one on a glass substrate for UV–vis spectroscopy and the other on an ITO/glass substrate for poling and in situ SHG measurement. One set was kept at room temperature in the dark overnight and the other was kept at 150 °C during the same period (about 16 h). A comparison of UV–vis spectra and SHG measured before and after this period revealed that no decay either in absorption or in $\chi^{(2)}$ occurred for the set of films kept at room temperature; whereas essentially equal decreases in absorption and $\chi^{(2)}$ were displayed by the set of films heated at 150 °C.

In the second experiment, polymer films were cured for 16 h at 120, 140, or 150 °C and then held at 100 °C for several days. UV–vis spectra were measured periodically to follow changes in peak absorption. The decay rate of the peak absorption was similar in all the films. In addition, the rate closely matched the decay in $\chi^{(2)}$ reported above for polymer films that had also been kept at 100 °C for several days.

The results of both of these experiments strongly suggest that the decrease in $\chi^{(2)}$ at 100 °C for the polymer film is due primarily to thermal degradation of the NLO-phore and that decay due to randomization of the dipolar orientation is negligible.

Measured Nonlinear Coefficients. SHG measurements on the polymer films poled at 1 MV/cm also allowed determination of second harmonic coefficients in these materials. A d_{33} value of 6.9 pm/V (relative to quartz: d_{11} = 0.5 pm/V) was obtained at a fundamental wavelength of 1.58 μm. Conversion to the E-O coefficient, using a simple two level model,[20] gave r_{33} of 3.3 pm/V at 1.3 μm. The E-O coefficient was also measured directly in transmission[21] using the output of a diode laser operating at 1.3 μm. The modulation frequency was 680 Hz and the modulating voltage ranged from 1.0 to 10.0 V_{rms}. The E-O response, which was linear over the entire voltage range, gave r_{33} of 3.6 pm/V.

Index Measurement. The refractive index of the polymer decreases on average by 0.004 upon hard-bake (150 °C for 16 h). This reduction in index is believed to be due to degradation of the NLO-phores by heat as explained above. After hard-bake, the average index at
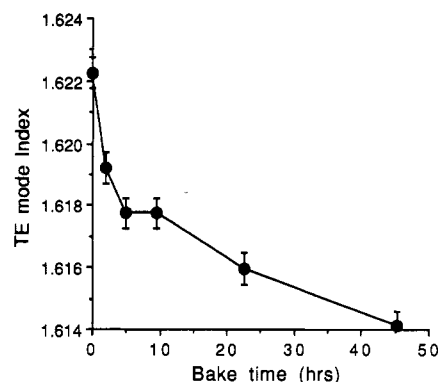

Figure 4. Refractive index of cross-linked polymer film derived from compound I measured at 1.3 μm as a function of bake time. The baking temperature was 150 °C.
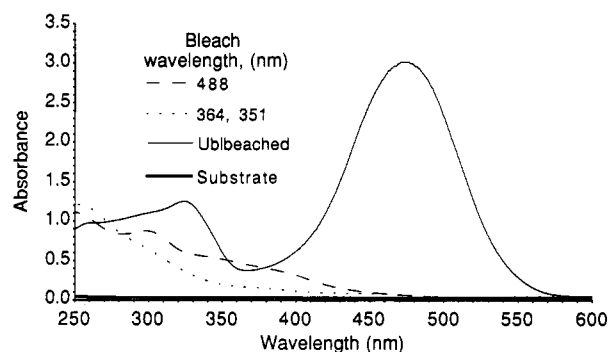

Figure 5. Absorption spectra of fully bleached cross-linked polymer film derived from compound I as a function of bleach wavelength.

1.3 μm was 1.611. The index of refraction decreased at a rate of 1.1×10^{-4} (°C)$^{-1}$ subsequent to the initial 4-h cure time as shown in Figure 4.

Photobleaching. Photobleaching of a dye-doped polymer causes the refractive index at 1.3 μm to decrease. This has made photobleaching a viable technique for fabrication of optical waveguides.[22] Complete bleaching of the polymer at different wavelengths results in different absorption spectra as shown in Figure 5, where the polymer is bleached using two different lines of an argon laser. The bleaching is irreversible and is a linear function of the incident beam intensity.[23] This suggests that the bleaching involves single-photon absorption.

Single-mode optical wave guides have been fabricated in the polymer by photobleaching using the 313-nm line of a Hg lamp source. The bleaching time is about 15 h at 8 mW/cm². The propagation loss at 1.3 μm is close to 1 dB/cm, which is essentially the loss measured for the polymer in a slab wave guide, indicating that photobleaching introduces very little additional propagation loss.

Single-mode channel wave-guide phase modulators were fabricated by a combination of photobleaching and poling. The wave-guide structure was poled at 1 MV/cm and cross-linked at 150 °C for 2 h followed by annealing at 100 °C for 14 h in the presence of the applied electric field. A maximum intensity modulation of 10 dB was observed from these modulators. An electrooptic coefficient of 3.3 pm/V was deduced from the π-phase shift of the modulator. This is in excellent agreement with the E-O coefficient

(20) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B* **1987**, *4*, 968.
(21) Van der Vorst, C. P. J. M.; Van Weerdenburg, C. J. M. *Proc. SPIE* **1990**, *1337*, 246.

(22) Rochford, K. B.; Zanoni, R.; Gong, Q.; Stegeman, G. I. *Appl. Phys. Lett.* **1989**, 1161.
(23) Moshrefzadeh, R. S.; Miesmer, D. K.; Radcliffe, M. D.; Francis, C. V.; Mohapatra, S. K. *Appl. Phys. Lett.* **1993**, *62*, 16.

determined from SHG measurements and also from direct measurement.

Summary

Step polymerization was utilized to synthesize a cross-linked polyurea–polyurethane NLO polymer. The films made from this polymer were of optical quality. Single-mode channel wave-guide phase modulators were fabricated by a combination of photobleaching and poling. The combined $\chi^{(2)}$ and absorptivity measurements suggest that the $\chi^{(2)}$ decay of this cross-linked polymer is primarily due to NLO-phore degradation and that orientational stability is apparently quite good for these materials. This in general points to the soundness of the cross-linking chemistry employed with these materials and the critical need for NLO-phores in poled polymers that are stable at high temperatures.