3472 Macromolecules 1994, 27, 3472-3477

Photo-Cross-Linking of a Polyurethane with Pendant Methacryloyl-Terminated 4-Alkoxy-4′-sulfamoylstilbene NLO Chromophores

Jody E Beecher, Tony Durst, Jean M. J. Fréchet,* and Adelheid Godt

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Craig S. Willand

Electronic Systems Division, Eastman Kodak Company, Rochester, New York 14650

Received January 25, 1994®

ABSTRACT: The photo-cross-linking of a polyurethane with pendant-oriented NLO chromophores terminated with methacryloyl groups has been achieved using free-radical photoinitiators. Due to the presence of *trans*-stilbene groups in the chromophore, the photo-cross-linking step must be restricted to the methacryloyl double bonds, proceeding without concurrent trans–cis isomerization of the stilbene. This can be achieved using an organometallic photoinitiator that absorbs at 532 nm. Due to the high temperature used to achieve poling of the NLO chromophores, addition of a hindered phenol is necessary to prevent the onset of thermal crosslinking. Imagewise photo-cross-linking of the oriented polymer can be used to produce a patterned material that exhibits a stable second-order NLO signal for several weeks at 100 °C.

Introduction

Polymers for devices based on electrooptic or second harmonic effects must have a stable, high second-order nonlinear optical (NLO) response. Polymers that exhibit second-order NLO properties require a noncentrosymmetric arrangement of the NLO active groups (chromophores). One method to achieve the needed order is to pole the chromophores with an electric field at or above the T_g of the polymer, and the "freeze in" the alignment by cooling the polymer below the T_g prior to switching off the electric field. This method of aligning the chromophores has afforded polymers with large NLO responses. However, over time or at elevated temperatures, the chromophores relax from the noncentrosymmetric arrangement and the NLO character of the polymer is lost.[1,2]

One method to avoid this instability is to create a network while poling by cross-linking the polymer. This approach "locks" the chromophores into place by reducing the mobility of the polymer segments. Stabilization of the poled orientation has been achieved by thermally induced cross-linking[3-10] such as curing of diepoxy/diamine systems,[3-5] diisocyanate/triol systems,[6] and polymers bearing acrylate groups.[8,9] Alternately, some improvement of stability has been achieved through photoinduced crosslinking via either a [2 + 2] cycloaddition of cinnamates,[11-13] a photoactivated reaction of benzophenone with butenyl side groups,[14] or a photocleavage of azides to nitrenes.[15] However, these photochemical crosslinking reactions are incompatible with chromophores based on stilbene or azobenzene groups since the photochemistry also affects the double bond of the chromophore itself.

One important distinction between photo-cross-linked systems and thermally cross-linked materials, is pattern delineation. Photo-cross-linking is inherently position-dependent by virtue of the fact that one can readily target specific areas of the sample for cross-linking and affect the solubility, thermal, and other material properties on a local scale. This patterning ability is commonly used in photoresist technology to facilitate the production of microelectronic devices for the semiconductor industry.

For nonlinear optical applications, the ability to pattern is critical for the production of complex poling patterns that may be required in some second-harmonic generation, as well as other, applications.[16] While poling patterns can be generated in thermally activated materials, these patterns are limited to those that can be produced through a single poling step, since any poling of these materials erases any previous poling process. Additionally, the creation of complex electrode patterns can lead to problems, such as conductivity breaks, that are related to temperature cycling. On the other hand, photo-cross-linking can be used to generate multiple poling steps using a single planar electrode, with the pattern complexity limited only by the exposure masks used.

The goal of the present work is to use photochemical cross-linking to stabilize the anisotropic alignment of the chromophores and to concurrently photoimage the polymers for device fabrication. Additionally, we have specifically targeted applications involving frequency doubling of laser diodes (800–850 nm). Such frequency doubling devices require material with optical transparency at both the laser (IR) and the second harmonic (blue) wavelengths, i.e. colorless materials. In a previous short communication,[17] we have reported on the second harmonic relaxation studies of a cross-linkable polymer that contains a pendant sulfonamide chromophore.[18] In this paper, we discuss the synthesis and characterization of a photo-cross-linkable polyurethane with NLO side chains, and the results from photo-cross-linking and electrooptic stability studies.

Results and Discussion

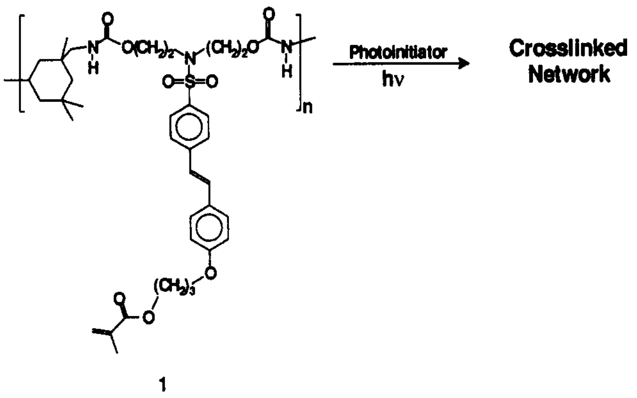
Our design for photopatternable NLO polymers is based on polymers containing reactive pendant groups that can be cross-linked using a photoinitiated radical process (Scheme 1). Polyurethane 1 has active side chains consisting of the NLO chromophore with a cross-linkable moiety at its extremity. This design requires the use of a bifunctional monomer with one end for the attachment to the polymer and the other end for the attachment of the cross-linkable group. On the basis of its relatively high NLO activity, low λ_{max}, and ease of synthesis, the

---

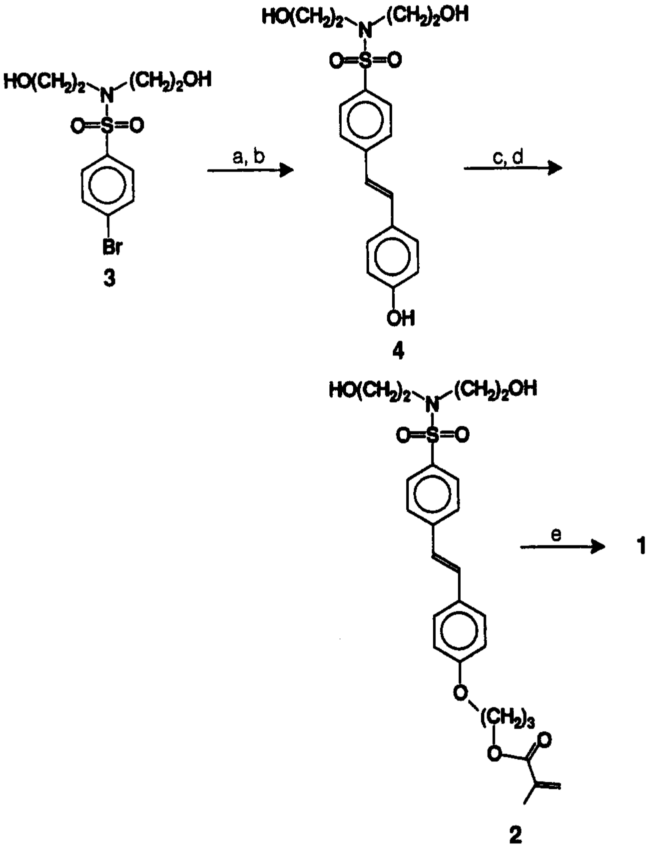
® Abstract published in *Advance ACS Abstracts*, May 15, 1994.

0024-9297/94/2227-3472$04.50/0

Scheme 1

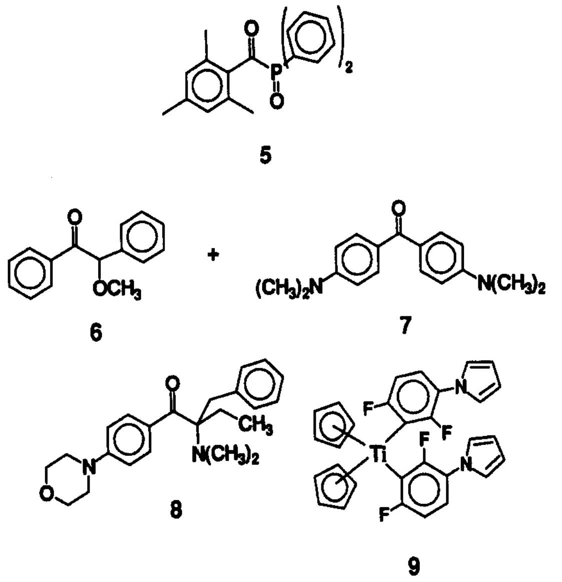


Scheme 2[a]



[a] (a) *t*-BOC-styrene/TEA/Pd(OAc)$_2$/P(*o*-tolyl)$_3$; (b) NaOMe/MeOH; (c) NaOH; (d) 3-bromopropyl methacrylate; (e) isophorone diisocyanate/DABCO.

Chart 1



sulfonamide chromophore[18] was chosen as the building block in our NLO active polymer. Monomer **2** (Scheme 2) contains a diol functionality allowing it to be polymerized in a classical step growth process while also providing reactive pendant vinyl groups for the eventual photoinitiated cross-linking.

Synthesis. Monomer **2** was synthesized by the Heck reaction[19] as outlined in Scheme 2. Aryl bromide **3** was coupled with 4-*tert*-butyloxycarbonyl)oxy]styrene in the presence of triethylamine and catalytic amounts of palladium diacetate and tri-*o*-tolylphosphine. Subsequent deprotection with sodium methoxide in methanol produced the deprotected stilbene **4**. Finally, the phenolate derivative of **4** was allowed to react with 3-bromopropyl methacrylate to give monomer **2** in 44% overall yield. Polymerization of monomer **2** with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate) in a step growth process is outlined in Scheme 1. This polymerization could not be achieved using the extremely active catalyst, dibutyltin dilaurate, due to the occurrence of a troublesome transesterification side reaction of the methacrylate moiety.[20] Therefore, the less-active catalyst, 1,4-diazabicyclo[2.2.2]octane was used to polymerize monomer **2** with isophorone diisocyanate. After purification by successive precipitation into ether and then into hexanes, polyurethane **1** (61% yield) was obtained with M_n = 5000, M_w = 7700.

DSC experiments indicate that the polymer undergoes a transition at 83 °C, which is assigned to the glass transition. The thermal degradation of the polymer, as studied in thermogravimetric analysis, begins at 305 °C. THF solutions of monomer **2** and polymer **1** show similar UV-vis spectra with an intense low-energy absorption band centered at 335 nm and a second absorption at 241 nm. The UV-vis spectrum of a thin film (2.7 μm) of the polymer on quartz shows an absorption cutoff at 402 nm.

Photopolymerization. Our objective was to create a thermally stable, cross-linked network through a photoinduced radical polymerization of the pendant methacrylate moieties. In view of the two types of reactive double bonds that are present in polyurethane **1**, it is important to select polymerization conditions that only involve the methacrylic double bonds while leaving the stilbene moieties intact. Additionally, a *trans* to *cis* photoisomerization,[21] either by direct or sensitized irradiation, must be avoided, since the *cis* isomer is significantly less efficient as a NLO chromophore than the *trans* isomer. Therefore, the photoinitiator used to cross-link the polymer must be photoactive outside the absorption region of the chromophore (absorbing to 400 nm), and isomerization of the stilbene chromophore must be avoided.

Various photoinitiators, that are sensitive to irradiation above 400 nm, were studied in the cross-linking reaction of polymer **1**. These photoinitiators (Chart 1) included 2,4,6-trimethylbenzoyldiphenylphosphineoxide (**5**),[22,23] 2-methoxy-2-phenylacetophenone (**6**) in the presence of the sensitizer 4,4′-bis(dimethylamino)benzophenone (**7**),[24] 2-benzyl-2-(*N*,*N*-dimethylamino)-1-(4-morpholinophenyl)-1-butanone (**8**),[23] and bis(η-5,2,4-cyclopentadien-1-yl)bis[2,6-difluoro-3-(1*H*-pyrrol-1-yl)phenyl]titanium (**9**).[23] The efficiency of the photoinitiators in the solid-state cross-linking reaction of polyurethane **1** was investigated by IR spectroscopy. Polymer films containing 5–10 wt % of the photoinitiator were irradiated in an inert atmosphere at elevated temperatures (100–150 °C). The changes in the

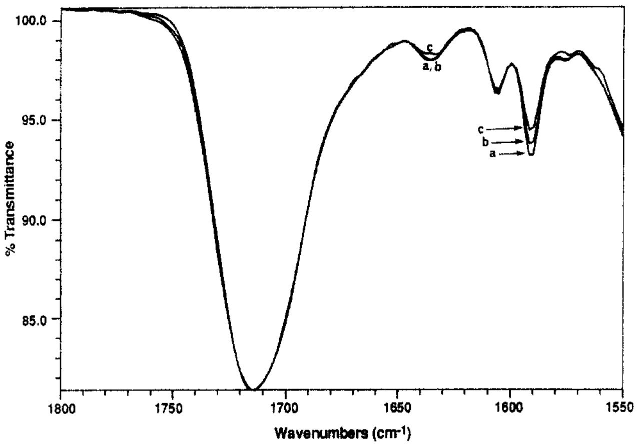


Figure 1. Change in infrared C=C absorptions of polyurethane film containing 8 wt % **5** with increasing radiation dose (400 nm, 110 °C). (a) Prior to irradiation; with irradiation of (b) 0.9, (c) 3.8 J/cm^2.

IR absorption bands of the methacrylate double bond (C=C stretching frequency: 1637 cm^{-1}) and the *trans*-stilbene double bond (C=C stretching frequency: 1591 cm^{-1}) were monitored before and after irradiation. Additionally, the *trans* to *cis* photoisomerization was investigated by comparing UV-vis absorption spectra before and after irradiation. In general, both *cis*- and *trans*-stilbenes have two strong UV absorption bands. *trans*-Stilbenes exhibit a strong absorption band at longer wavelengths and a weaker absorption band at the shorter wavelengths. The reverse is true of the *cis* isomer for which the shorter wavelength absorption band is stronger than the longer absorption band.[21]

The infrared absorption spectrum of an irradiated film (400 nm, 0.9 J/cm^2, 110 °C) of polymer **1** in the presence of photoinitiator **5** showed no change in the C=C stretching frequency of the methacrylate double bond and a decrease ($\sim$12%) in the C=C stretching frequency of the *trans*-stilbene moiety (Figure 1). The UV-vis spectrum of a similarly treated sample exhibited a decrease ($\sim$8%) in the absorption band at 334 nm and slight increase ($\sim$4%) in the absorption band at 242 nm (Figure 2). These absorption changes are consistent with a *trans* to *cis* isomerization of some of the stilbene groups. The IR spectrum of an irradiated polymer film in the absence of the photoinitiator shows only a small change (<2%) in the intensity of the stilbene C=C stretching frequency. Hence the loss of the stilbene may well be due to a sensitization of the stilbene by the photoinitiator. Additionally, longer irradiations of polymer films with photoinitiator **5** at the same or higher temperatures (up to 130 °C) cause even greater losses of the stilbene moiety while leading to only minimal decreases in the methacrylate double bond. For example, irradiation (400 nm, 3.8 J/cm^2, 110 °C) of polymer **1** in the presence of photoinitiator **5** causes a 30% decrease in the C=C stretching frequency of the stilbene moiety and only a 5% decrease in the C=C stretching frequency of the methacrylate double bond (Figure 1). Hence, photointiator **5** is clearly not suitable for the photoinitiated radical cross-linking reaction of polyurethane **1**. The photoinitiating systems involving **6**–**8** were similarly ineffective. Each of these systems caused an isomerization of the stilbene chromophore, which was deemed to be unacceptable in view of our goals of NLO activity.

In contrast, photoinitiator **9** proved to be useful in the photopolymerization of polymer **1**. Irradiation (532 nm, 1.2 J/cm^2, 150 °C) of polymer **1** in the presence of photoinitiator **9** produced an insoluble film. The infrared absorption spectrum showed a decrease ($\sim$25%) in the C=C stretching frequency of the methacrylate double bond and only a slight decrease ($\sim$5%) in the *trans*-stilbene moieties (Figure 3). Also observed was a shift of the C=O stretching frequency from 1717 to 1720 cm^{-1}, which is consistent with a loss in conjugation due to the reaction of the methacrylate double bond. Increasing the radiation dose to 3.2 J/cm^2 increases the cross-link density, as revealed by a large decrease in the methacrylate double bond region ($\sim$40%). However, the irradiation dose also causes a $\sim$20% loss in the *trans*-stilbene double bond region (Figure 3). The UV-vis spectrum of a similarly treated film exhibited a decrease in both the absorption band at 334 nm ($\sim$19%) and the lower energy band at 242 nm ($\sim$7%) (Figure 4). This decrease in both absorption bands indicates that, in this case, the loss of the *trans*-stilbene moiety is not due to a photoisomerization. Instead, the reduction of the *trans*-stilbene is most likely caused by a radical reaction of the stilbene double bond.[25] This is supported by the following observations: the UV-vis of a polymer film containing 5 wt % AIBN heated to 100 °C in vacuum for 12 h shows a decrease in both of the absorption bands, while no change is seen in a control experiment at 100 °C in the absence of AIBN.

Imaging. In view of our goal to photopattern the NLO polymer while concurrently stabilizing the poled chro-

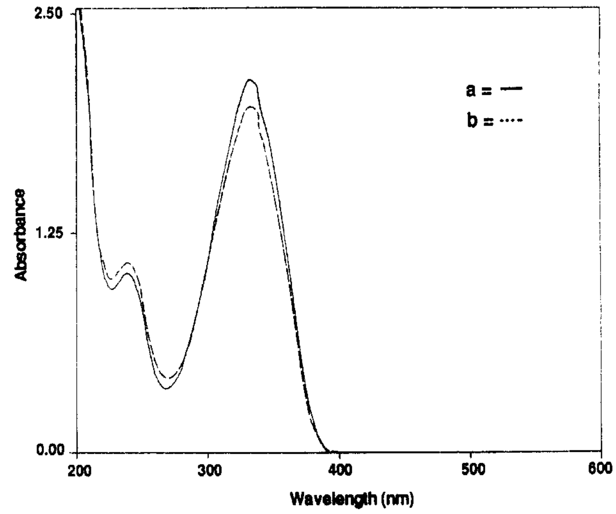


Figure 2. Change in UV-vis absorptions of polyurethane film containing 8 wt % **5**. (a) Prior to irradiation; (b) with irradiation of 0.9 J/cm^2 (400 nm, 110 °C).

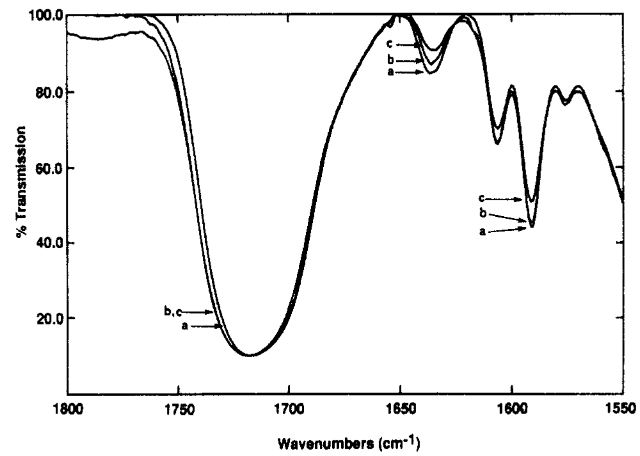


Figure 3. Change in infrared C=O and C=C absorptions of polyurethane film containing 10 wt % **9** with increasing radiation dose (532 nm, 150 °C). (a) Prior to irradiation; with irradiation (b) 1.2, (c) 3.2 J/cm^2.

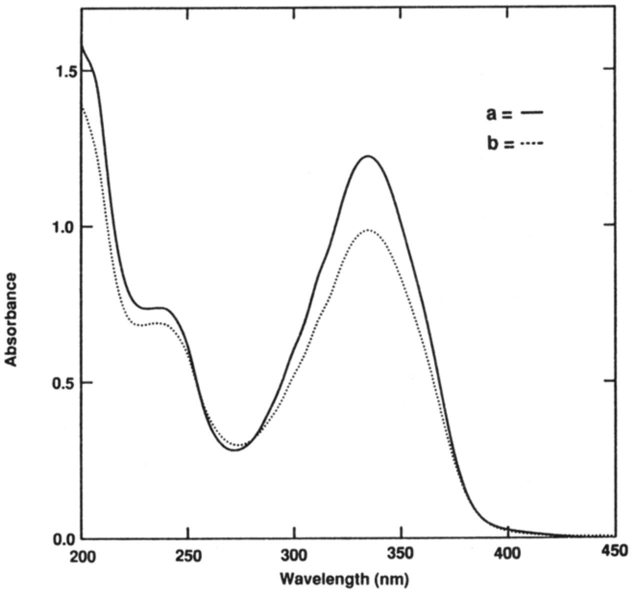


Figure 4. Change in UV-vis absorptions of polyurethane film containing 10 wt % **9**. (a) Prior to irradiation; (b) with irradiation of 3.2 J/cm^2 (532 nm, 150 °C).

mophores, it is important that no thermal cross-linking reaction occurs under the conditions used for the poling and photo-cross-linking steps. We have previously shown[17] that some thermal cross-linking occurs when the polymer film is heated to the poling temperature (150 °C). However, this thermal event can be almost completely eliminated by incorporating 0.5 wt % of a hindered phenol radical inhibitor, 2,2-bis[[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate (Irganox 1010). Therefore, using standard photolithographic techniques in combination with this thermal inhibitor, the cross-linking reaction can be exclusively confined to exposed regions of the polymer film and can be achieved simultaneously with the poling step. This allows for any image development step that would be required in device fabrication.

To demonstrate this, the polymer film containing 10 wt % of photoinitiator **9** and 0.5 wt % of Irganox 1010 was irradiated at 532 nm (3.9 J/cm^2) and at 150 °C through a mask with 5-μm features. For the purposes of illustration, the pattern was developed in 2-propanol:chloroform (1:1 v/v). The scanning electron micrograph of the resulting image is shown in Figure 5.

The photo-cross-linking process occurred as expected resulting in a developed polymer film that faithfully reproduced the pattern of the exposure mask. In this case, the resolving power of the process, i.e. the smallest feature attainable, is clearly determined by the mask. In actual device fabrication, the development step could be eliminated and the photo-cross-linking step repeated several times on a poled sample, with the final processing step involving a flood exposure to fully cross-link the film in the absence of the electric field.

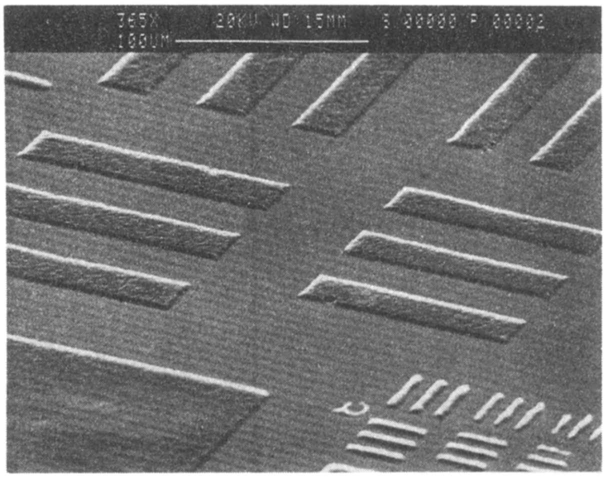


Figure 5. Scanning electron micrograph of negative tone image.

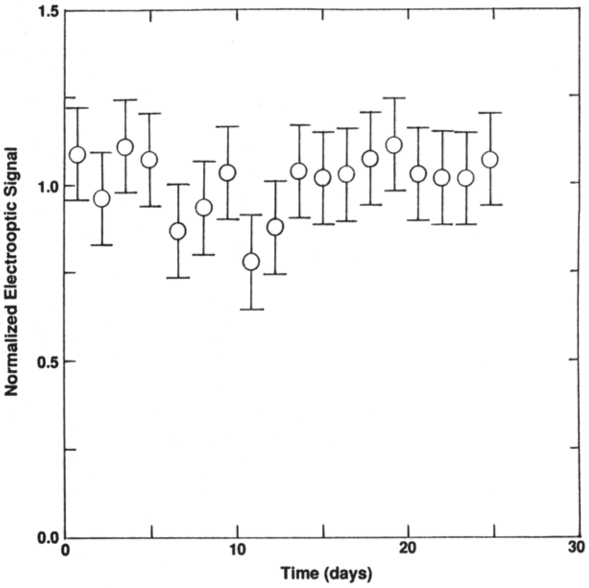


Figure 6. Normalized electrooptic signal as a function of time at 100 °C.

Electrooptic Experiments. The effect of the cross-linking on the long-term stability of the NLO response was monitored using the electrooptic (EO) effect. A polymer film containing 10 wt % photoinitiator **9** and 0.5 wt % Irganox 1010 was heated to 150 °C and simultaneously poled (50 VDC) and irradiated (532 nm, 4.2 J/cm^2). The sample was slowly cooled to 100 °C before removal of the poling field. The electrooptic coefficient (r_{33} = 0.5 pm/V at 633 nm) at 100 °C was then measured as a function of time. The normalized electrooptic signal for the cross-linked polymer film is depicted in Figure 6. There is little orientational relaxation occurring, even over the period of 30 days. This is in sharp contrast to the results for the uncross-linked film at a similar temperature. In that case, the experimental temperature is much higher than the glass transition temperature (85 °C), and the orientational relaxation time would be expected to be on the microsecond scale. Therefore, the net effect of the cross-linking is to *significantly* shift the orientational relaxation time at 100 °C.

Conclusions

We have shown through UV and IR experiments that polyurethane **1** can be photochemically cross-linked without significantly affecting the NLO chromophores. In addition, we have successfully demonstrated simple photoimaging capabilities of our NLO polymer. Micrometer-scale patterns that faithfully reproduced the features of the exposure mask were generated and developed.

The long-term orientational stability at elevated temperatures displayed by these photo-cross-linked systems represent some of the best results published to date. This stability is crucial for integrated optic applications which may require short-term stability during processing at elevated temperatures, e.g. wire bonding as well as long-term stability at operating temperatures. Better results may be achievable using higher cross-linking temperatures; however, a problem of chemical stability may need to be addressed under these conditions. Clearly more studies need to be performed to optimize the poling and cross-linking conditions before practical optical devices based on such photopolymers can be produced.

Experimental Section

Photopolymerization Studies. For the IR studies, solutions of 18–22 wt % 1 in 1,2,3-trichloropropane (TCP) containing 5–10 wt % (referring to the amount of polymer) photoinitiator were filtered through a 0.5-μm filter (Millipore, Millex-SR) and then spincast onto NaCl substrates, at 2000 rpm to give 2.0–2.5 μm thick films. For the UV-vis studies, the solution concentrations ranged from 3–5 wt % and were spincast onto quartz substrates at 3000 rpm to give ca. 0.25 μm thick films. The films were baked at 110 °C for 15 min to evaporate residual solvent. The film thicknesses were determined on an Alpha step 200 instrument. All irradiations were done under an inert atmosphere. Polymer films containing photoinitiator 5–8 were irradiated with a 350-W Hg lamp through a 400-nm interference filter (10-nm bandpass). Polymer films containing photoinitiator 9 were irradiated with either a 350 W Hg lamp through a 436 nm interference filter (10 nm bandpass) or with a frequency-doubled cw mode locked Nd: YAG laser at 532 nm. Infrared spectra were obtained with a Nicolet IR/44. The peak heights of the methacrylate double bond absorbance (1637 cm^{-1}) and the *trans*-stilbene double bond absorbance (1591 cm^{-1}) were normalized with respect to the carbonyl absorbance (1719 cm^{-1}) to adjust for any variances in the film thickness. UV-vis spectra were obtained on a Perkin Elmer Lambda 6 or a Nicolet 9430 UV-Visible spectrophotometer.

Electrooptic Measurements. Indium tin oxide (ITO)-covered glass substrates (2.5 × 2.5 cm) were dipped halfway into hydroiodic acid (55 % in water; 50 °C), for 30 s to remove the ITO coating, polished with 0.5-μm aluminum oxide paste, cleaned with detergent, and carefully rinsed with water. Solutions of 22 wt % of polymer 1 in 1,2,3-trichloropropane (TCP) containing 2 wt % photoinitiator 9 were stirred overnight before being filtered through a 0.5-μm filter (Millipore, Millex-SR). The resultant solutions were immediately spincast onto ITO-coated glass substrates at 2000 rpm to give ca. 2.5-μm thick films. After baking the films at 96 °C and 0.03 torr for 12–15 h to remove residual solvent, dumbbell-shaped electrode (50 Å chromium, 1000 Å gold) were deposited.

The electrooptic setup used was similar to that of Schildkraut.[26] The sample was mounted in a nitrogen-purged temperature chamber and an AC voltage (20 VAC p-p @ 1 kHz) was applied to the electrodes. Linearly-polarized light (1 mW, 633 nm or 830 nm) from a HeNe laser was passed through a variable-phase retardation plate and directed onto the sample. The reflected light beam was passed through a polarizer, interference filter, and detected by a photodiode. The resultant photodiode signal modulated at the applied voltage frequency (1 kHz) was detected using a Lockin amplifier. The electrooptic signal was determined by normalizing the modulated photodiode signal to the laser intensity (DC photodiode signal).

Synthesis. All experiments were carried out under nitrogen or argon. The starting materials were purchased from Aldrich and used without purification except isophorone diisocyanate and methacryloyl chloride which were distilled under vacuum (110 °C/0.1 mmHg and 0 °C/10 mmHg, respectively). 3-Bromopropyl methacrylate was made according to literature[27] and purified by distillation (46–52 °C/0.25 mmHg). The photoinitiators (5, 8, and 9) and radical inhibitor (Irganox 1010) were gifts from Ciba-Geigy. Solvents were dried following standard procedures.[28] All compounds can be easily spotted on TLC silica plates containing a fluorescent dye (Merck, Kieselgel 60 F_{254}). Merck Kieselgel 60 (230–400 mesh) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM300 spectrometer (300 MHz and 75 MHz, respectively) using deuteriochloroform as a solvent and an internal standard, except as stated. Signal assignments were made on the basis of literature data.[29,30] All coupling constants are in hertz. UV-vis spectra were recorded in THF on a Perkin Elmer Lambda 6 UV-visible spectrophotometer. IR spectra were obtained on a Nicolet IR/44 from KBr pellets or as polymer films on NaCl disks. The melting points are uncorrected. DSC measurements were obtained on a Mettler DSC 30 instrument with a heating rate of 10 °C/min. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analyses were measured on a Mettler TG50 thermobalance with a heating rate of 20 °C/min. Gel permeation chromatography (GPC) was obtained using three 5-μm Hewlett-Packard columns (330 × 7.7 mm) connected in series in order of increasing pore size (100 Å, 500 Å, 1000 Å; flow rate 1 mL/min; 40 °C) with a Wyatt Technology Corp. DAWN F laser photometer and a Waters 410 differential refractometer; data analysis was performed with ASTRA software, version 2.02.

***N,N*-Bis(2-hydroxyethyl)-4-bromobenzenesulfonamide (3).** A solution of 4-bromobenzenesulfonyl chloride (5.0 g, 19.6 mmol) in $CHCl_3$ (60 mL) was added dropwise to diethanolamine (6.19 g, 58.9 mmol) in $CHCl_3$ (45 mL). After stirring at rt for 18 h the reaction mixture was poured into ice-cold water and the precipitate was filtered off. The $CHCl_3$ phase was washed several times with water, dried over magnesium sulfate, concentrated under reduced pressure, and combined with the vacuum-dried precipitate. Recrystallization from $CHCl_3$ gave 5.25 g (83%) of colorless 3: mp 99–101 °C; ^{1}H NMR δ 3.19 (s, 2H, OH), 3.28 (t, J = 5.6, 4H, CH_2N), 3.83 (t, J = 5.6, 4H, CH_2O), 7.69 (AA′BB′, 4H, CH); ^{13}C NMR δ 52.8, 62.1, 127.9, 128.8, 132.5, 137.4; IR 3308 (br), 1339, 1167 cm^{-1}. Anal. Calcd for $C_{10}H_{14}BrNO_4S$: C, 37.05; H, 4.35; N, 4.32; Br, 24.65; S, 9.89. Found: C, 37.24; H, 4.59; N, 4.34; Br, 24.81; S, 10.02.

4-Hydroxy-4′-[*N,N*-bis(2-hydroxyethyl)sulfamoyl]stilbene (4). A mixture of 3 (3.00 g, 9.25 mmol), 4-[(*tert*-butoxycarbonyl)oxy]styrene (t-BOC-styrene) (3.04 g, 13.9 mmol), palladium(II) acetate (0.021 g, 0.09 mmol), tri-*o*-tolylphosphine (0.085 g, 0.28 mmol), and triethylamine (1.40 g, 13.9 mmol) in dry acetonitrile (65 mL) was refluxed for 3 days. After removing the solvent in vacuo, the residue was redissolved in $CHCl_3$, washed with water, and dried over $MgSO_4$. The crude product, a mixture of *t*-BOC-substituted product and the final product, was dissolved in THF and treated with sodium methoxide in methanol (0.64 g/30 mL). Aqueous workup and recrystallization from acetonitrile yielded 2.71 g (81%) of 4: mp 210–211 °C; ^{1}H NMR (acetone-d_6) δ 3.27 (t, J = 5.6, 4H, CH_2N), 3.74 (m, 4H, CH_2O), 4.24 (t, J = 5.7, 2H, OH), 6.87, 7.50 (AA′BB′, 4H, 3-, 5-H, 2-, 6-H), 7.14 (d, J = 16.3, 1H, C*H*═CH), 7.36 (d, J = 16.3, 1H, CH═C*H*), 7.74, 7.81 (AA′BB′, 4H, 2′-, 6′-H, 3′-, 5′-H); ^{13}C NMR (acetone-d_6) δ 53.0, 62.1, 116.5, 124.6, 127.3, 128.2, 128.9,129.3, 132.6, 143.2, 158.8, 206.1; IR 3250 (br), 1328, 1155 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_5S$: C, 59.49; H, 5.82; N, 3.85; S, 8.82. Found: C, 59.50; H, 5.99; N, 3.88; S, 8.88.

4-[(3-Methacryloylpropyl)oxy]-4′-[*N,N*-bis(2-hydroxyethyl)sulfamoyl]stilbene (2). A suspension of stilbene 4 (25.0 g, 68.8 mmol) and NaOH (2.76 g, 69.0 mmol) in methanol (350 mL) was stirred at 50 °C until all NaOH was dissolved. After removal of the methanol in vacuo, the residue was dissolved in DMF (65 mL) and added dropwise to a solution of 3-bromopropyl methacrylate (16.0 g, 77.4 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (0.07 g, 0.3 mmol) in DMF (40 mL). After 12 h of stirring at rt, water was added and the precipitate was filtered off. Flash chromatography ($CHCl_3$/MeOH 10:1 v/v), followed by recrystallization ($CHCl_3$/hexanes 4:1 v/v), gave 22.3 g (66%) of colorless 2: mp 101–102 °C; ^{1}H NMR δ 1.93 (s, 3H, CH_3), 2.17 (m, 2H, $CH_2CH_2CH_2$), 2.36 (bs, 2H, OH), 3.28 (t, J = 4.8, 4H, CH_2N), 3.87 (m, 4H, HOC*H*$_2$), 4.08 (t, J = 6.2, 2H, $PhOCH_2$), 4.34 (t, J = 6.2, 2H, CH_2OOC), 5.55, (s, 1H, CH), 6.09, (s, 1H, CH), 6.89, 7.45 (AA′BB′, 4H, 3-, 5-H, 2-, 6-H), 6.96 (d, J = 16.3, 1H, C*H*═CH), 7.16 (d, J = 16.3, 1H, CH═CH), 7.58, 7.75 (AA′BB′, 4H, 2′-, 6′-H, 3′-, 5′-H); ^{13}C NMR δ 18.3, 29.0, 52.9, 61.9, 62.0, 65.2, 115.5, 125.3, 125.6, 127.3, 128.4, 129.1, 130.3, 132.2, 137.2, 137.9, 142.9, 160.0, 167.3; UV-vis λ_{max} (log ϵ) = 241 (3.884), 337 nm (4.209); IR 3341 (br), 1712, 1705, 1639, 1592, 1334, 1155 cm^{-1}. Anal. Calcd for $C_{25}H_{31}NO_7S$: C, 61.33; H, 6.38; N, 2.86; S, 6.55. Found: C, 61.15; H, 6.28; N, 2.85; S, 6.44.

Polyurethane 1. To isophorone diisocyanate (1.6682 g, 7.505 mmol) in dry THF (75 mL) were added at rt 2 (3.6743 g, 7.505 mmol), 2,6-di-*tert*-butyl-4-methylphenol (0.15 g, 0.67 mmol), and finally diazabicyclo[2.2.2]octane (0.226 g, 2.0146 mmol). The solution was refluxed for 10 d. After quenching with 5 mL of dry methanol and stirring for 1 h at rt, the polymer was successively precipitated into diethyl ether and hexanes: yield 3.28 g (61%) of colorless 1: ^{1}H NMR (DMSO-d_6) δ 0.59–1.15 (m, 13H), 1.31–1.57 (m, 2H), 1.86 (s, 3H, $CH_2{=}CCH_3$), 2.07 (br s, 2H, $CH_2CH_2CH_2$), 2.70 (br s, 2H, CH_2NH) 3.35 (br s, 4H, NCH_2CH_2O), 3.47, 3.49 (2 s, together 1H, CHNH), 3.55 (br s, 2H, NH) 4.06 (br. s, 6H, CH_2OPh and $NCH_2C_{H2}O$), 4.24 (s, 2H, $COOCH_2CH_2CH_2$), 5.66 (s, 1H, vinyl CH_2), 6.03 (s, 1H, vinyl CH_2), 6.95, 7.39 (AA′BB′, 4H, arom H), 7.16, (d, J = 16.4, 1H, vinyl CH), 7.35, (d, J = 16.4, 1H, vinyl CH), 7.74 (AA′BB′, 4H, arom H); ^{13}C NMR (DMSO-d_6) δ 18.0, 23.1, 27.0, 27.4, 29.9, 31.2, 34.9, 35.6, 35.7, 41.2, 44.0, 45.5, 46.6, 47.6, 51.5, 54.4, 61.3, 62.2, 64.4, 114.7, 124.4, 125.7, 126.8, 127.4, 128.3, 129.2, 131.4, 135.8, 136.4, 141.9, 154.9, 156.4, 158.7, 166.5; UV-vis λ_{max} (log ϵ) = 242 nm (4.173), 332 nm (4.295); values of ϵ are calculated relative to the repeating unit); IR 1719, 1637, 1591 cm^{-1}. Anal. Calcd for $(C_{37}H_{49}N_3O_9S)_n$: C, 62.43; H, 6.94; N, 5.90; S, 4.50. Found: C, 62.16; H, 6.87; N, 6.13; S, 4.37. M_n = 5,000, M_w = 7,700; T_g = 85 °C.

Acknowledgment. Financial support of this research by the Office of Naval Research and the Eastman Kodak Co. is acknowledged with thanks. Thanks are also due to the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship and to the University of Ottawa for the granting of a sabbatical leave (to T. Durst).

References and Notes

(1) Starling, E. G. J. *Recl. Trav. Chim. Pays-Bas.* **1991**, *110*, 492 and refs therein.
(2) Burland, D. M.; Miller, R. D.; Reiser, O.; Twieg, R. J.; Walsh, C. A. *J. Appl. Phys.* **1992**, *71*, 410.
(3) (a) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241. (b) Jungbauer, D.; Reck, B.; Twieg, R.; Yoon, D. Y.; Willson, C. G.; Swalen, J. D. *Appl. Phys. Lett.* **1990**, *56*, 2610. (c) Zentel, R.; Jungbauer, D.; Twieg, R.; Yoon, D. Y.; Willson, C. G. *Makromol. Chem.* **1993**, *194*, 859.
(4) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mat.* **1989**, *1*, 167.
(5) Kim, K. I.; Kim, S. C. *Polym. Bull.* **1992**, *29*, 393.
(6) (a) Chen, M.; Dalton, L. R.; Yu, L. P.; Shi, Y. Q.; Steier, W. H. *Macromolecules* **1992**, *25*, 4032. (b) Shi, Y.; Steier, W. H.; Chen, M.; Yu, L.; Dalton, L. R. *Appl. Phys. Lett.* **1992**, *60*, 2577.
(7) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 225.
(8) Xu, C.; Wu, B.; Dalton, L. R.; Shi, Y.; Ranon, P. M.; Steier, W. H. *Macromolecules* **1992**, *25*, 6714.
(9) Allen, S.; Bone, D. J.; Carter, N.; Ryan, T. G.; Sampson, R. B.; Devonald, D. P.; Hutchings, M. G. in *Organic Materials for Nonlinear* Optics *II*; Hann, R. A., Bloor, D. R., Eds.; Royal Soc. *Chem.*: Cambridge, 1991; p 235.
(10) Yu, L.; Chan, W.; Dikshit, S.; Bao, Z.; Shi, Y.; Steier, W. H. *Appl. Phys. Lett.* **1992**, *60*, 1655.
(11) (a) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. *Appl. Phys. Lett.* **1991**, *58*, 2459. (b) Mandal, B. K.; Kumar, J.; Huang, J.-C.; Tripathy, S. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 63.
(12) Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421.
(13) Müller, H.; Müller, I.; Nuyken, O.; Strohriegl, P. *Makromol. Chem. Rapid Commun.* **1992**, *13*, 289.
(14) (a) Kawatsuki, N.; Pakbaz, K.; Schmidt, H.-W. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 625. (b) Kawatsuki, N.; Pakbaz, K.; Schmidt, H.-W. *J. Appl. Polym. Sci.* **1993**, *50*, 1575.
(15) Hayashi, A.; Goto, Nakayama, M.; Sato, H.; Watanabe, T.; Miyata, S. *Macromolecules* **1992**, *25*, 5094.
(16) Khanarian, G.; Norwood, R. A.; Haas, D.; Feuer, B.; Darim, D. *Appl. Phys. Lett.* **1992**, *57*, 977.
(17) Beecher, J. E.; Fréchet, J. M. J.; Robello, D. R.; Willand, C. S.; Williams, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 12216.
(18) Beecher, J. E.; Durst, T.; Fréchet, J. M. J.; Godt, A.; Pangborn, A.; Robello, D. R.; Willand, C. S.; Williams, D. J. *Adv. Mat.* **1993**, *5*, 632.
(19) Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2454.
(20) Tomita, K.; Ida, H. *Polymer* **1975**, *16*, 185.
(21) Meier, H. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1399.
(22) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141.
(23) Rutsch, W.; Angerer, H.; Desobry, V.; Dietliker, K.; Husler, R. In *Proceedings of the 16th International Conference in Organic Coatings Science and Technology*, July 9–13, 1990, Athens, Greece; Patsis, A. V., Ed.; Technomic: Lancaster, 1990; p 423.
(24) Gruber, H. F. *Prog. Polym. Sci.* **1992**, *17*, 953.
(25) Bevington, J. C.; Huckerby, T. N. *Macromolecules* **1989**, *18*, 176.
(26) Schildkraut, J. S.; *Appl. Opt.* **1990**, *29*, 2839.
(27) Combellas, C.; Petit, M. A.; Thiébault, A.; Froyer, G.; Bosc, D. *Makromol. Chem.* **1992**, *193*, 2445.
(28) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1988.
(29) Pretsch, E.; Clerc, T.; Siebl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1989.
(30) Wendisch, D.; Reiff, H.; Dieterich, D. *Angew. Makromol. Chem.* **1986**, *141*, 173.