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Concurrent Stabilization and Imaging of a Novel Polymer for Second Harmonic Generation via *In Situ* Photopolymerization

by Jody E. Beecher, Jean M.J. Fréchet,
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13. ABSTRACT *(Maximum 200 words)*

The simultaneous patterning and stabilization of a polyurethane designed for its use in second harmonic generation has been achieved by photoinduced crosslinking of a poled film containing a titanocene photoinitiator. The crosslinked polymer shows good clarity and its NLO response remains stable for several weeks at 100°C.

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Concurrent stabilization and imaging of a novel polymer for second harmonic generation via *in situ* photopolymerization.

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Materials for devices based on electrooptic or second harmonic effects must have stable, high second order nonlinear optical (NLO) response.[1,2] The noncentrosymmetric arrangement necessary in order to observe a response has been achieved by poling polymers containing NLO chromophores. However, over time or at elevated temperatures, the chromophores are able to relax from the oriented alignment and the second order NLO properties of these materials are lost. Stabilization of the poled orientation can be achieved by crosslinking the polymer either thermally[3-10] or photochemically.[11-13] A significant advantage of photochemical crosslinking is the ability to directly create devices using photo-imaging techniques. While some improvement of stability has been achieved through photo-induced crosslinking via a [2+2]cycloaddition of cinnamates[12] and via photo-cleavage of azides to nitrenes,[13] neither photochemistry is compatible with the desirable chromophores that are based on stilbene or azobenzene moieties. Our goal is to use photochemical crosslinking both to stabilize the anisotropic alignment of the chromophores and, concurrently, to photo-image the polymers for the direct fabrication of devices. An additional challenge of our target of NLO polymers for the frequency doubling of laser diode light in the range of 800-900 nm is that it requires materials that are optically transparent at both the fundamental and half wavelengths, i.e. colorless materials.

We have designed the colorless polyurethane **1** for its ability to be crosslinked using a photoinitiated radical process. Polymer **1** has side chains consisting of the NLO chromophore with a highly active crosslinkable moiety at its extremity. This design requires the use of a bifunctional NLO chromophore with one end designed for its attachment to the polymer and the other end for the attachment of the photocrosslinkable group. Therefore, monomer **2** containing a donor acceptor stilbene chromophore[14] with alkoxy as the donor moiety and sulfonamide as the acceptor moiety has been synthesized.[15] Polymerization of **2** with isophorone diisocyanate in the presence of diazabicyclo[2.2.2]-octane affords the desired soluble polyurethane **1** (Scheme 1).

Since isomerization of the *trans* stilbene to the *cis* stilbene significantly reduces the efficacy of the chromophore, the photocrosslinking conditions must not cause a photoisomerization, either by direct or sensitized irradiation. The photoinitiator used to crosslink the polymer must therefore be photoactive outside the absorption region of the chromophore and must not sensitize the stilbene chromophore. We have found that the titanocene photoinitiator **3** meets both of these requirements, in addition, it is also reported to bleach upon photoreaction.[16] The photocrosslinking reaction of a film of polyurethane **2** containing 10 wt% of photoinitiator **3** was monitored by IR spectroscopy (Figure 1). The C=C stretching frequency of the methacrylate group at 1636 cm^{-1} decreased upon exposure to light, while the C=C stretching frequency of the *trans* stilbene moiety at 1590 cm^{-1} remained essentially unchanged[17]. Additionally, a shift from 1717 cm^{-1} to 1721 cm^{-1} in the carbonyl absorption corresponding to a loss of conjugation was observed.

The stability of the NLO response of a poled polymer can be studied by monitoring the intensity of the second harmonic (SH) signal with increasing temperature. For example a poled polymer may exhibit SH generation at room temperature, but, as the temperature of the polymer is increased to near its glass transition (T_g), the chromophores gain increasing mobility and reorient to a lower energy isotropic arrangement with concomitant loss of the SH signal. The temperature range at which the SH signal is lost is indicative of the stability of the NLO alignment. At constant heating rate, the derivative of the SH signal with respect to temperature is proportional to the number of chromophores relaxing at that temperature. This derivative provides a direct measure of the orientational relaxation distribution of the chromophores. For comparison purposes, we define T_{max} as the temperature at which the greatest amount of orientational relaxation is occurring, i.e., the peak of the temperature derivative of the SH signal, or alternately, the inflection point in the curve showing the loss of SH signal.

In view of our goal to photopattern the NLO polymer while concurrently stabilizing the poled chromophores, it is important to ensure that no thermal crosslinking reaction occurs under the conditions used for the poling and photocrosslinking steps. Therefore, we have studied the relaxation of the polymer after it was poled at 90 °C, after it was poled at 150 °C, and after it was poled and irradiated at 150 °C (Figure 2).[18] Non-irradiated films that had been poled at 90 °C show a rapid decay of SH intensity (Fig. 2a) upon heating above 55 °C with T_{max} reached at 82 °C, a temperature that corresponds to T_g for the uncrosslinked polymer. Poling the films containing the photoinitiator at 150 °C causes an increase of 37°C in the value of T_{max}, indicating that some thermal crosslinking has occurred (Fig. 2c). This thermal crosslinking reaction is essentially eliminated, even at 150 °C, by incorporating a hindered phenol, tetrakis[methylene-(3,5-di-tert-butyl-4-hydrocinnamate)]methane (Irganox1010®), into the polymer films to inhibit the formation of radicals (Fig. 2b). Irradiation of polymer films, containing the photoinitiator and the inhibitor, at 150 °C raises T_{max} to 130°C (Fig. 2d). In view of the control experiments described above, this increase in T_{max} can be attributed exclusively to a photo-induced crosslinking reaction. The photocrosslinking reaction not only serves to stabilize the orientation of the NLO chromophores but it also provides for patterning. As a result, the significant increase in T_{max} value obtained upon photocrosslinking affords a useful process window for any image development step that would be required in device fabrication. The scanning electron micrograph (Figure 3) shows an image created by irradiating the polymer at 150 °C through a mask with features of the order of 5 µm, followed by image development.

Long-term stability studies of the photocrosslinked films poled at 150°C show that the NLO response remains high and essentially unaffected over the course of several weeks at 100°C. Evaluation of these new photopatternable NLO materials for use in periodic poled waveguides will be carried out shortly.

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(15) N,N-Bis(2-hydroxyethyl)-4-bromophenylsulfonamide was coupled with *t*-BOC-styrene in the presence of triethylamine and catalytic amounts of palladium diacetate and tri-o-tolyl phosphine. Subsequent deprotection with sodium methoxide in methanol produced 4-(Hydroxy)-4'-[N,N-bis(2-hydroxyethyl)-sulphamoyl]stilbene. Removal of the phenolic proton of the stilbene with NaOH and reaction with 3-bromopropylmethacrylate gave monomer (**2**) in 44% overall yield.

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(17) In contrast, other photoinitiators such as 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide or 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone caused extensive trans to cis isomerization and the peak at 1590 cm^{-1} was observed to decrease considerably.

(18) For details on sample configuration see: Köhler, W.; Robello, D. R.; Dao, P. T.; Willand, C. S.; Williams, J. D. *J. Chem. Phys.* **1990**, *93*, 9157.

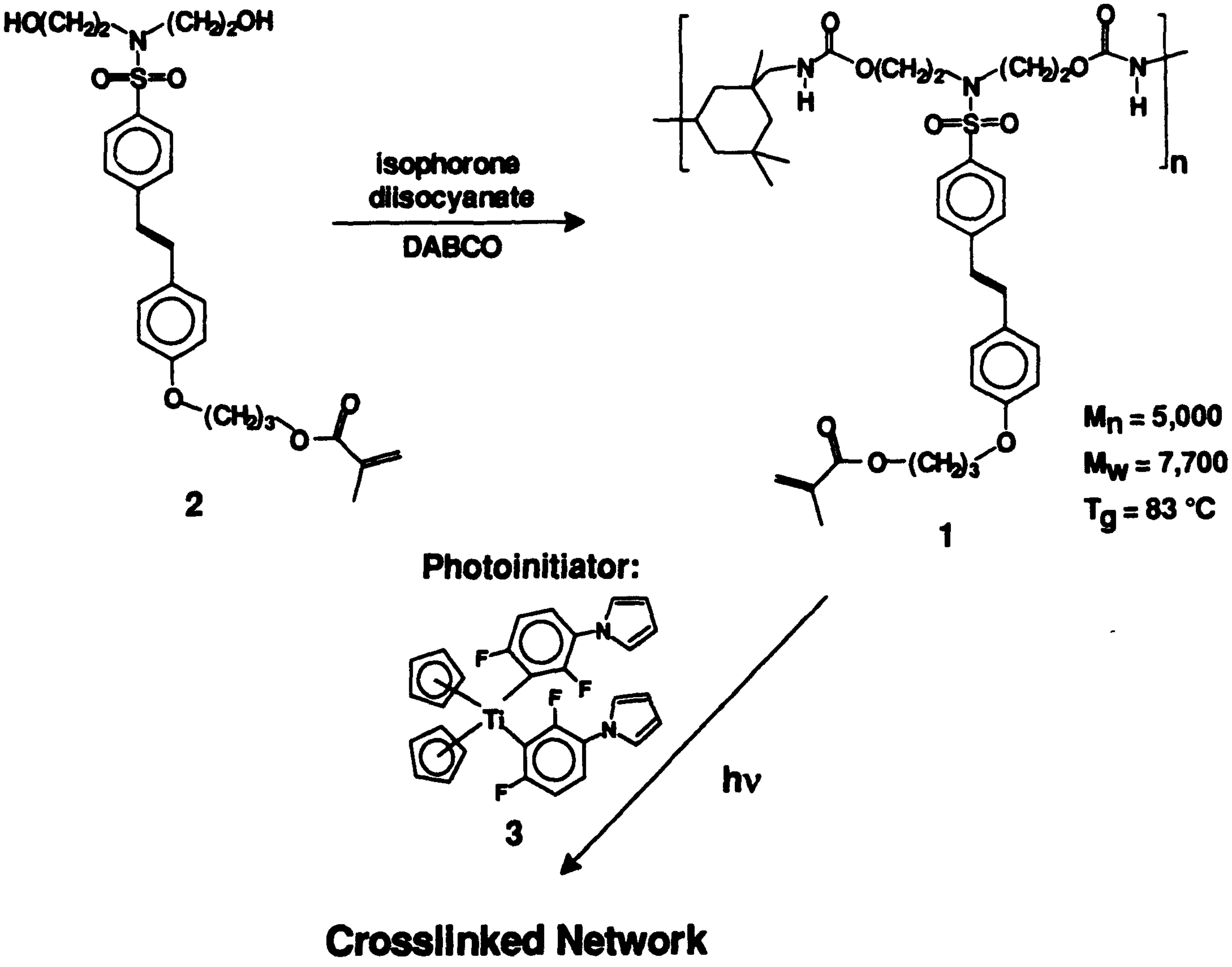
Figure Captions

Figure 1 IR spectrum for double bond region for polymer films (1 µm thick) containing 10 wt % of photoinitiator (**3**). (a) Before irradiation (b) After irradiation at 150 °C with 350 W Hg lamp (436 nm filter, 2 J/cm^2).

Figure 2. *Lower curve:* SH intensity decay ($\lambda_{\text{fundamental}}$ = 1064 nm) for polymer films (ca. 2.5 µm) containing 10 wt % of photoinitiator **3**; *upper curve:* temperature derivative. All samples were heated at 5 °C/min to poling temperature, poled with 40 V for 5 min, cooled to 30 °C at 5 °C/min, and reheated at 3 °C/min while recording the SH intensity. **(a)** sample poled at 90 °C; **(b)** sample containing 0.5 wt% Irganox 1010® poled at 150 °C; **(c)** sample poled at 150 °C in the absence of inhibitor, **(d)** sample containing 0.5 wt% Irganox 1010® poled at 150 °C and irradiated with a frequency-doubled cw modelocked Nd:YAG laser (532 nm, 4 J/cm^2)

Figure 3 Scanning electron micrograph of negative-tone image obtained by irradiation (532 nm, 4J/cm^2, 150 °C) of polymer film (ca. 2.5 µm thick) containing 10 wt % photoinitiator and 0.5 wt% Irganox 1010® and developed in isopropanol/chloroform 1:1(v/v).

Scheme 1


HO(CH2)2 N (CH2)2OH
O=S=O
O (CH2)3 O O
2
isophorone diisocyanate
DABCO
N H O O(CH2)2 N (CH2)2O O N H
O=S=O
n
O O (CH2)3 O
1
Mn = 5,000
Mw = 7,700
Tg = 83 °C
Photoinitiator:
F F N Ti F N F
3
hν
Crosslinked Network

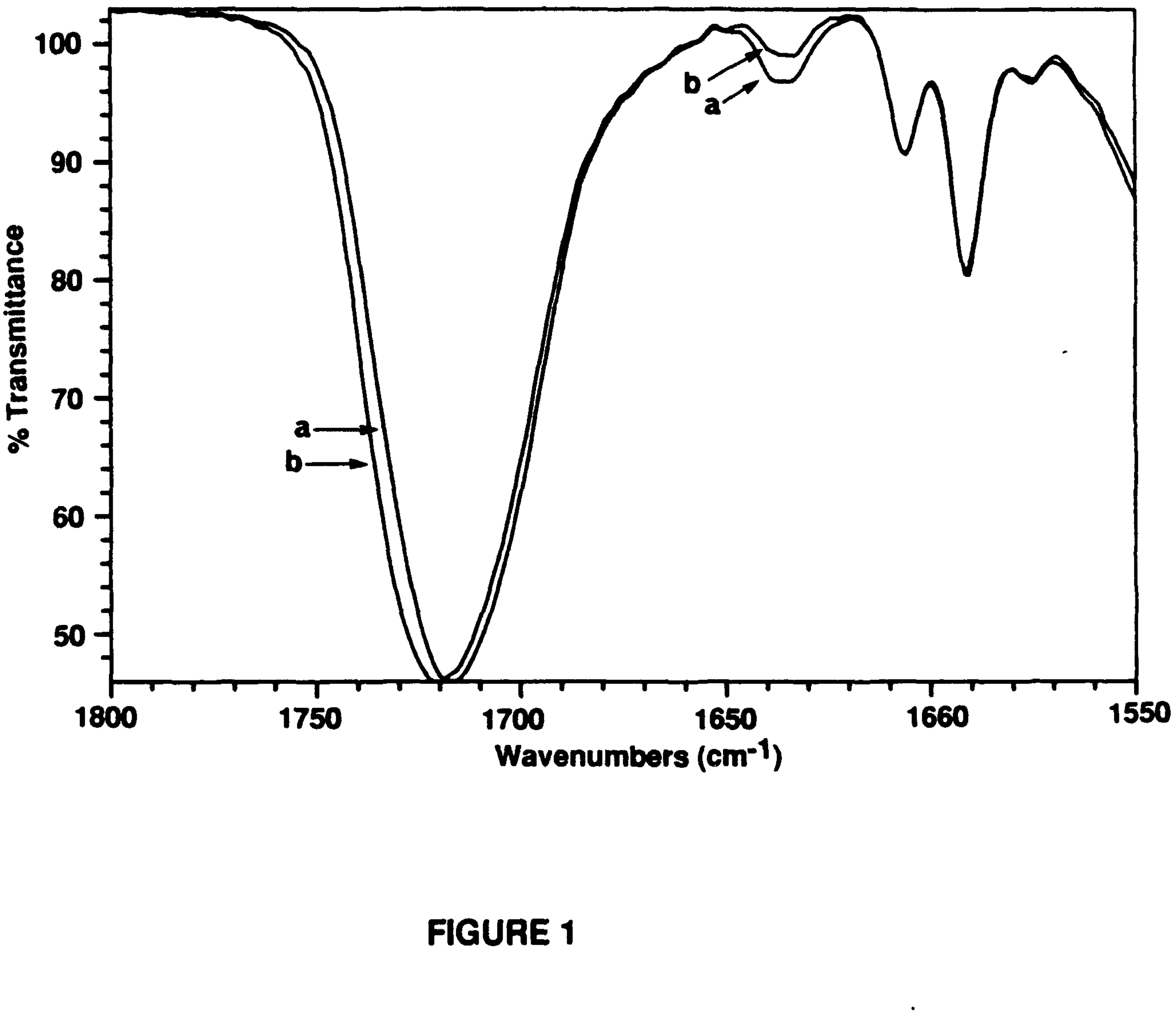

100
90
80
70
60
50
% Transmittance
1800
1750
1700
1650
1660
1550
Wavenumbers (cm-1)
a
b
b
a

FIGURE 1

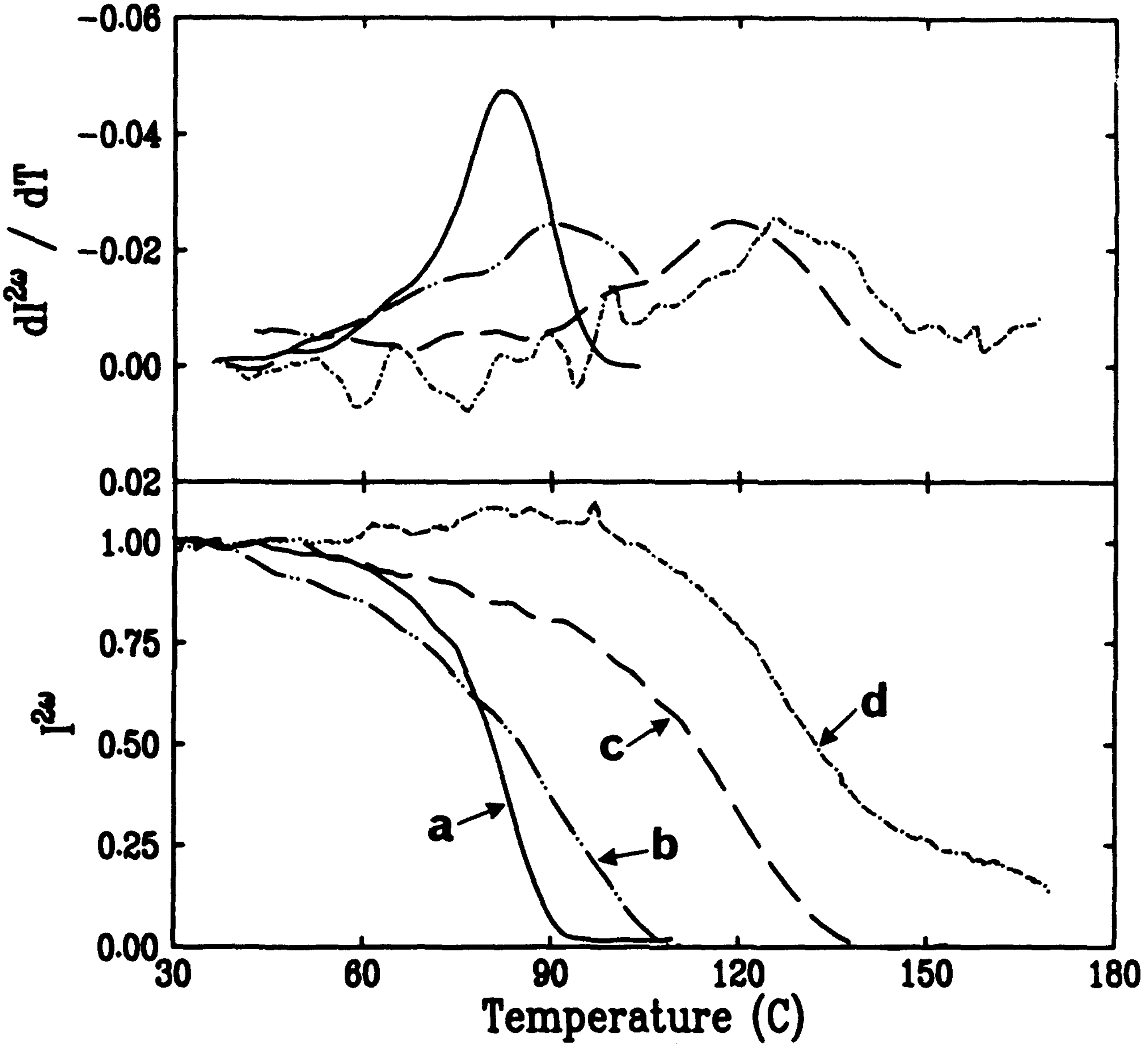

-0.06
-0.04
-0.02
0.00
0.02
$dI^{2\omega} / dT$
1.00
0.75
0.50
0.25
0.00
$I^{2\omega}$
a
b
c
d
30
60
90
120
150
180
Temperature (C)

FIGURE 2

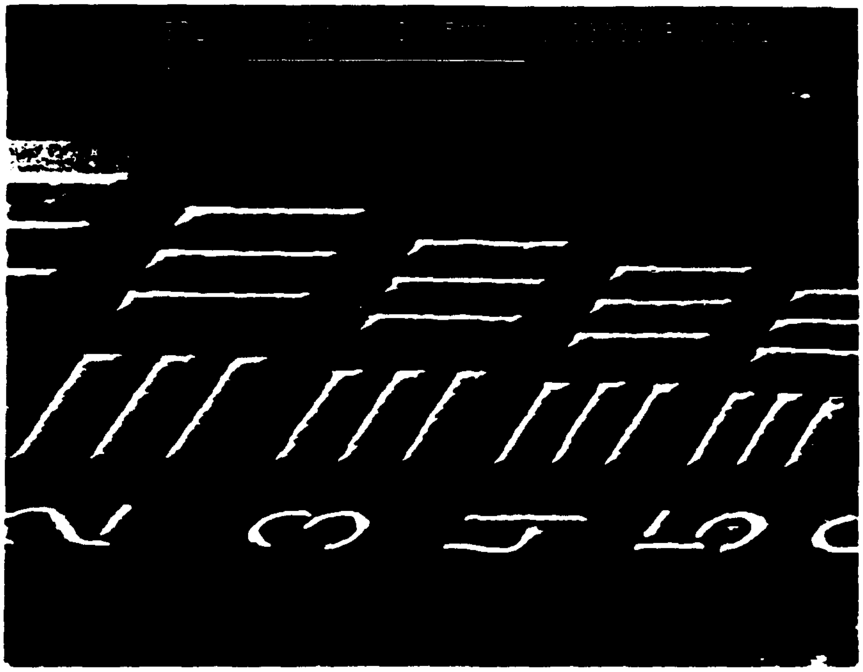


FIGURE 3

Photoimaging of oriented polymers for non-linear optics: Preparation and photocrosslinking of a novel photopolymer containing a polymerizable double-bond attached to a side-chain NLO chromophore

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ABSTRACT: The design of a novel type of photocrosslinkable polymer containing NLO chromophores in its side-chain has been explored. The photopolymer is based on a clear polyurethane backbone with pendant chromophore groups terminated by a polymerizable double bond that can be used to crosslink a film of the NLO photopolymer once it has been oriented by a classical poling process. The photocrosslinking is achieved by irradiation of films containing a small amount of a photobleachable radical photoinitiator: 2,4,6-trimethyl-benzoyldiphenylphosphine oxide. The effect of photocrosslinking on the mobility of the chromophores has been studied by recording the intensity of the frequency doubled light, generated by a poled sample, with increasing temperature. The SH signal for the photocrosslinked polymer shows excellent stability demonstrating that the approach may be used to generate complex poling patterns for practical NLO applications, such as the frequency doubling of diode IR lasers.

Introduction

Novel polymers for optoelectronics designed for the frequency doubling of laser light must include several properties and features in addition to those responsible for the non-linear optical (NLO) behavior of the materials. For example, the polymers must have excellent physical, optical, and mechanical properties that allow their use as a thin transparent film or as an object of the desired shape. In addition, a new organic polymer used for frequency doubling

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Photocrosslinking of Oriented Polymers for Non-linear Optics: Preparation and Photocrosslinking of a Novel Photopolymer Containing a Polymerizable Double-Bond Attached to a Side-Chain NLO Chromophore

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The design of a novel type of photocrosslinkable polymer containing NLO chromophores in its side-chain has been explored. The photopolymer is based on a clear polyurethane backbone with pendant chromophore groups terminated by a polymerizable double bond that can be used to crosslink a film of the NLO photopolymer once it has been oriented by a classical poling process. The photocrosslinking is achieved by irradiation of films containing a small amount of a photobleachable radical photoinitiator: 2,4,6-trimethyl-benzoyldiphenylphosphine oxide. The effect of photocrosslinking on the mobility of the chromophores has been studied by recording the intensity of the frequency doubled light, generated by a poled sample, with increasing temperature. The SH signal for the photo-crosslinked polymer shows excellent stability demonstrating that the approach may be used to generate complex poling patterns for practical NLO applications, such as the frequency doubling of diode IR lasers.

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must allow for both the anisotropic arrangement of the NLO chromophores, and also for the retention of this arrangement over the entire lifetime of the device in which it is incorporated.[1,2)] The required order may be achieved simply through poling with an electric field near or above the glass transition temperature (T_g) of the polymer. Finally, in order to "freeze" this alignment into place, the polymer is cooled below its T_g before switching off the field.[2,3)]

The long-term stability of the chromophore alignment achieved through electric field poling and, therefore, the stability of the second order NLO properties, are dependent on the difference between the T_g and the use temperature: the larger the difference, the better the stability.[4)] However, it is extremely difficult to prepare high T_g polymers that can be processed without causing the decomposition of the delicate NLO units that it contains. In addition, the efficiency of the poling process decreases with increasing poling temperature.[2,4)]

One promising avenue involves the formation of a polymer network through a crosslinking reaction that occurs while the NLO chromophores are maintained in an aligned state. This approach allows the use of a polymer of moderate T_g, that can be easily poled, later increasing the T_g through the crosslinking reaction. The crosslinking reduces the mobility of the polymer segments and, consequently, the mobility of the chromophores. Either thermal or photochemical techniques can be used to achieve the necessary crosslinking. Previous work by other groups has focused mainly on thermally induced crosslinking,[5-17)] involving for example systems such as the curing of diepoxy-diamine systems,[5-9)] diisocyanate-diol (or triol),[10-13)] or diisocyanate-diamine[14)] systems, or of polymers bearing acrylate[15,16)] or ethynyl[17)] groups. Alternately, photoinduced crosslinking via a [2+2]cycloaddition of cinnamates,[18-21)] a photo-activated reaction of benzophenone with butenyl side groups,[22)] or a photocleavage of azides to nitrenes and their subsequent reactions[23)] has been used.

Formation of the network by photochemical crosslinking offers the ability to create complex patterns through standard photolithographic techniques. This is a significant advantage over thermal crosslinking reactions, particularly with regard to fabrication of integrated optical devices. However, the photocrosslinking step often causes a direct or sensitized *trans* to *cis* isomerization of stilbene or azobenzene based NLO chromophores, significantly decreasing the NLO activity of these chromophores.[21)] We have recently reported,[24)] one system that can be photocrosslinked without isomerization of the stilbene NLO chromophores. Another appealing alternative is to exploit chromophores based on diphenyl acetylene (tolane) moieties that cannot isomerize but are, nonetheless, strongly active. In this paper, we report on a crosslinkable polymer **1**, containing 4-alkoxy 4'-sulfamoyl substituted tolane chromophores, its synthesis, characterization, and its use in photocrosslinking experiments.

Results and Discussion

The design selected for the photopolymer includes a polymer backbone with side-chains consisting of the tolane-containing chromophores each terminated by a polymerizable end-group. Synthetic considerations led us to select a main-chain obtained by a step-growth process, and chain-ends consisting of polymerizable double bonds. The position of these polymerizable groups at the end of the side chains containing the chromophores is important to provide for the long-term stabilization of the latter once they have been oriented. Following crosslinking by a free-radical photoinitiated process, the rigid rod-like NLO active moieties are attached at both of their extremities which restricts their mobility and contributes to the preservation of their long-term orientation.

Recently, a similar NLO polymer has been synthesized and crosslinked, resulting in high stability of the NLO signal.$^{15)}$ However, the crosslinking in this case was achieved via a thermally intitiated radical polymerization. In contrast, our aim is to accomplish the crosslinking by photochemical means.

In addition to creating photo-crosslinkable polymers with a stable NLO response, another goal of this work is to produce polymers for frequency doubling of laser diode light (800 - 850 nm). This demands materials that are transparent at both the fundamental and half wavelength, i.e. colorless materials. In previous work with low molecular weight compounds for second order NLO applications we have shown that the 4-alkoxy 4'-sulfamoyl substituted tolane **2** is colorless and has a sufficiently high nonlinear susceptibility.$^{25)}$ Therefore, polyurethane **1** with a side-chain tolane linked at one of its extremities to the backbone through a sulfonamide group, and at the other to a *vinylbenzyloxy pendant moiety was prepared.*

Synthesis.

Polymer **1** was prepared by the reaction of diol **3** with diisocyanate **4** (Scheme 1). The key step in the synthesis of diol **3** (Scheme 2) is the building of the tolane structure. It was achieved using the versatile coupling chemistry$^{26,27)}$ of alkynes with aryl halides in the presence of a catalytic amount of Pd (II) and copper(I) iodide. In a first step, the donor substituted aryl iodide **5**, prepared from 4-(chloromethyl)styrene and 4-iodophenol, was allowed to react with trimethylsilylacetylene to give alkyne **6**. Desilylation to compound **7** and subsequent coupling of compound **7** with the acceptor substitued aryl iodide **8** gave diol **3** in an overall yield of 61% with respect to compound **5**.

Refluxing equimolar amounts of diol **3** and 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane **4** (isophorone diisocyanate) in THF with dibutyltin dilaurate as a catalyst gave the completely soluble (THF,

$CHCl_3$) and colorless polyurethane **1**. Diisocyanate **4** was used as a 3:1 mixture of a *trans* and a *cis* isomer28) (^1H NMR). Reaction of diol **3** with *trans*-1,4-cyclohexyl diisocyanate or 1,6-hexamethylene diisocyanate under the conditions described above produced materials that were insoluble in THF or cold DMSO. A similar polyurethane obtained by the reaction of diol **3** with tolyl diisocyanate (2,4- and 2,6-isomers in a 4:1 ratio) was also soluble in THF and $CHCl_3$, but less so than polymer **1**. However, this polyurethane was not studied further because of its inconsistent thermal behavior varying from run to run during DSC experiments.

The structure of polymer **1** is confirmed by ^1H and ^{13}C NMR spectroscopy. All ^{13}C signals can be assigned based on the NMR data for diol **3**, data given in the literature for urethanes derived from diisocyanate **4**,28) and the results of a DEPT (distorsionless enhancement by polarization transfer) experiment. Based on the DEPT spectrum of polymer **1** it is assumed that the ^{13}C NMR signals of C-1 and C-2 in reference 28 have to be exchanged with each other. All signals of the ^1H NMR spectrum are broadened, especially those assigned to the protons of the polymer main-chain (0-4.5 ppm). The chemical shifts of all ^1H NMR signals are in agreement with literature data29) and correlate with those observed for diol **3**. The polyurethane isolated by a typical precipitation process was very slightly contaminated by a low molecular weight impurity as evidenced by the presence of additional very weak signals in the ^1H NMR spectrum. These extra signals appear either as low-field shoulders or, in the case of the signal at 5.02 ppm, as a very small separate signal at 5.07 ppm. The ^1H NMR spectrum of the filtrate from the polymer precipitation process consisted of two species with lower molecular weight than **1** (GPC) and showed signals corresponding to those of the trace impurities in the precipitated polymer.

Characterization of Polyurethane 1.

The GPC trace of a representative sample of the polymer taken after quenching the polyaddition reaction with a small amount of dry methanol and before further work-up steps, such as precipitation of the polymer, reveals the presence of several low molecular species and a bimodal distribution of the polymer. This distribution is fully reproducible but the cause of the bimodal distribution has not been clarified. In particular, detailed NMR analyses of the polymer showed no evidence of products originating from the well known side reactions that may occur during urethane formation.28) The relative molecular weights of the polymers prepared by reaction of **3** and **4** obtained by GPC with polystyrene calibration were quite high. Therefore, the polymer used in all NLO experiments was precipitated twice from a THF solution into methanol giving a material with M_n = 17000 and M_w = 163000.

The UV-VIS spectrum of the polymer in THF (Fig. 1) shows an absorption band at 310 nm and one at 254 nm. Based on a comparison of the UV-VIS spectra of compounds **1**, **2**, **3** and **9** in THF (Fig. 1), the absorption band at 310 nm is assigned to the donor-acceptor substituted tolane unit and the band at 254 nm to the styrene moiety. Compounds **2** and **9**, that do not contain a styrene moiety, show only an absorption maximum around 310 nm while diol **3** and polymer **1**, which both have a pendant styrene group, show an additional absorption maximum at 254 nm. Compound **9** was prepared for comparison purposes using the same procedure as used for diol **3**. The absorption of 0.5 μm thick polymer films on quartz cuts off at 374 nm.

DSC measurements show that the polymer undergoes a transition at 100 °C which is assigned to the glass transition. When polymer **1** is heated above 200 °C, a strongly exothermic transition is observed. After a DSC scan up to 260 °C, the material is intensely yellow and insoluble in THF, $CHCl_3$, DMSO or

DMF, indicative of a crosslinking reaction. UV experiments on polymer films coated on quartz discs revealed a 5-8% decrease of the styrene absorption at 254 nm after heating the films at 200 °C for 30 - 60 min. In contrast, no change in the absorption band at 310 nm assigned to the tolane moiety was observed, although it is estimated that changes as low as 1% would be detected. This suggests that the styrene moiety, rather than the triple bond is responsible for the observed thermally induced crosslinking.

The thermal degradation of the polymer under nitrogen recorded by TGA with a heating rate of 10 K/min starts at 300 °C and is only completed beyond 650 °C. It proceeds in two steps with an inflection point at around 480 °C corresponding to a loss of 49%.

Photocrosslinking.

2,4,6-Trimethylbenzoyldiphenylphosphine oxide (**10**) was chosen as photoinitiator for the crosslinking experiments. It is reported both to be an effective initiator in the free radical polymerization of styrene30,31) and to undergo photobleaching.30,32) The UV-VIS spectrum of compound **10** shows a low intensity, but distinctive absorption centered at 380 nm (log ε = 2.76) and tailing well above 400 nm.30) To achieve a colorless, crosslinked end product, the photobleaching of **10** is an important prerequisite. Since the polymer itself absorbs rather strongly as shown in Figure 1, the absorbancy of **10** at longer wavelengths is necessary because it allows efficient photoinitiation without interference from the polymer. Exposure at longer wavelength is also required to avoid side-reactions involving the chromophore itself. For example, flood exposure of a hot melt of the colorless model25) chromophore **2** under argon resulted in an intensely yellow material. The same yellowing is observed by flood exposure at 110-120 °C of a polymer film without photoinitiator. In contrast, control experiments without irradiation gave no change in color or solubility. Therefore, the crosslinking experiments were carried out using a 50-nm bandpass filter centered at 400 nm.

The photoinitiator **10** was used as the commercially available 1:1 mixture with 2-hydroxy-2-methyl-1-phenylpropan-1-one (**11**), called Darocur® 4265 (**12**). Compound **11** itself absorbs light well below 400 nm and does not act as a primary photoinitiator in these experiments because of the light filter used.

To test the photo-crosslinking of the polyurethane **1**, films (1-3 μm thick) of the polymer containing 7-8 wt % of photoinitiator **12** were irradiated (30 min; 4.0 mW/ cm^2 at 400 nm) under argon at 110-120 °C. Under these conditions the films became insoluble and non-swelling, indicative of a photo-crosslinking reaction. In addition, these films also became faintly yellow in appearance, although no measurable difference could be observed in their UV-vis spectra. In contrast, polymer films containing photoinitiator **12** that were only heated at 110-120 °C, and not irradiated, remained completely soluble and colorless. In this case, no crosslinking occurs, excluding the possibility of thermal crosslinking at this temperature. However, as discussed earlier, thermal crosslinking does occur when the polymer is heated to higher temperatures.

Monitoring of the photocrosslinking step by spectroscopic techniques proved difficult due to the very low intensity of the signals under observation. UV-vis experiments show a small decrease of the styrene absorption band and no change in the tolane absorption region. While the change in UV absorption could not be quantified accurately, the polymer film is modified by photoirradiation to an extent that is sufficient to have an appreciable effect its physical characteristics (solubility, toughness).

Second Harmonic Stability.

The effect of crosslinking on the orientational relaxation of the chromophores was studied next, using the property of poled samples to double the frequency of light. This can be done by recording the second harmonic (SH) signal decay either with time at a constant temperature (below T_g) or with increasing temperature.33) We chose the latter method in which, upon heating, a poled sample shows an SH signal decay in a specific temperature range, depending on the sample and its history. This temperature range is a measure of the stability of the induced chromophore orientation. Crosslinking is expected to stabilize the chromophore alignment and therefore to shift this temperature range towards higher temperatures.

The sample configuration was the same as described by Köhler et al.34) 1.6 μm thick films of the polyurethane containing 7 wt % of photoinitiator **12** were spincast onto a glass plate covered with a conductive indium tin oxide (ITO) layer on half of its area. On top of the polymer film a dumbbell shaped gold electrode was vapor deposited. The samples were mounted inside a nitrogen purged oven. The experiments involved the following steps carried out in succession: (1) heating the sample to the poling temperature, (110 °C - 130 °C, i.e. above its glass transition temperature T_g) at a rate of 20 °C/min; (2) applying a DC voltage of -50V to the gold electrode (ITO electrode grounded) while maintaining the poling temperature, then heating further to the final crosslinking temperature; (3) irradiating the sample at this temperature for 30 min with light of a 200 W mercury lamp using the light filter mentioned above (6-10 mW/cm^2 at 400 nm); (4) cooling the sample at a rate of 5 °C/min to 50 °C and removing the applied voltage; (5) recording the SH signal intensity $I_{2\omega}$ of laser light ($\lambda_{\text{fundamental}}$ = 1064 nm) while reheating the sample at a rate of 4 °C/min. In those instances where the films were not irradiated, cooling was usually started about 4 min after the final temperature had been reached. We studied the relaxation of nonirradiated and irradiated samples as a function of different poling and irradiation temperatures. In order to compare the results we refer to the temperature T_{50} at which $I_{2\omega}$ is decreased by 50%. The accuracy of the determination of T_{50} is estimated to be ± 2 °C.

Nonirradiated films that had been poled at 130 or 150 °C showed a rapid decay of $I_{2\omega}$ starting around 90 °C with a T_{50} at 107 °C (Fig. 2a). In the case of these uncrosslinked films, the mobility is closely related to the polymer's glass transition temperature (100 °C as determined by DSC). As expected, irradiation at temperatures of 130, 150 and 170 °C raised the T_{50} of the samples by 13, 26 or 45 °C, respectively (Fig. 2b-d). At 130 °C, this shift in T_{50} can be attributed exclusively to a photoinduced crosslinking reaction. This is supported by the observation that a nonirradiated sample, heated and poled at 130 °C for 30 min, shows an increase in T_{50} of only 2 °C while retaining its solubility in THF.

However, the shift in T_{50} observed when the polymers are irradiated at higher temperatures is caused by a contribution of both thermal and photochemical crosslinking reactions. For example, a nonirradiated polymer film held at 170 °C shows an increase of about 10 °C in T_{50} value and is only partially soluble, clearly indicating that some thermally induced crosslinking takes place. Nonetheless, there is an appreciable difference in T_{50} (35 °C) between the irradiated and non-irradiated films. As observed in earlier experiments, at even higher temperatures, (209 °C for 30 min) purely thermal crosslinking results in an even greater shift of T_{50} (70 °C).

Conclusions.

This work demonstrates that a colorless functional NLO polymer that can be crosslinked by an efficient photochemical radical polymerization can be designed and prepared. While some faint yellowing of the crosslinked polymers was observed, this change was too small to be quantified by UV-vis spectroscopy using 1-3 μm thick films. The SH measurements show that the photocrosslinking of the NLO polymer creates materials that possess a highly stabilized chromophore orientation. Therefore, T_{50} was increased by 10-35 °C, depending on the irradiation temperature. Although, there is some thermally induced crosslinking, this contribution is relatively small at irradiation temperatures of 170 °C or below,. As a result of the increase in T_{50} this system has great potential for the photochemical generation of the sort of complex poling patterns that are needed for state of the art applications of non-linear optics.

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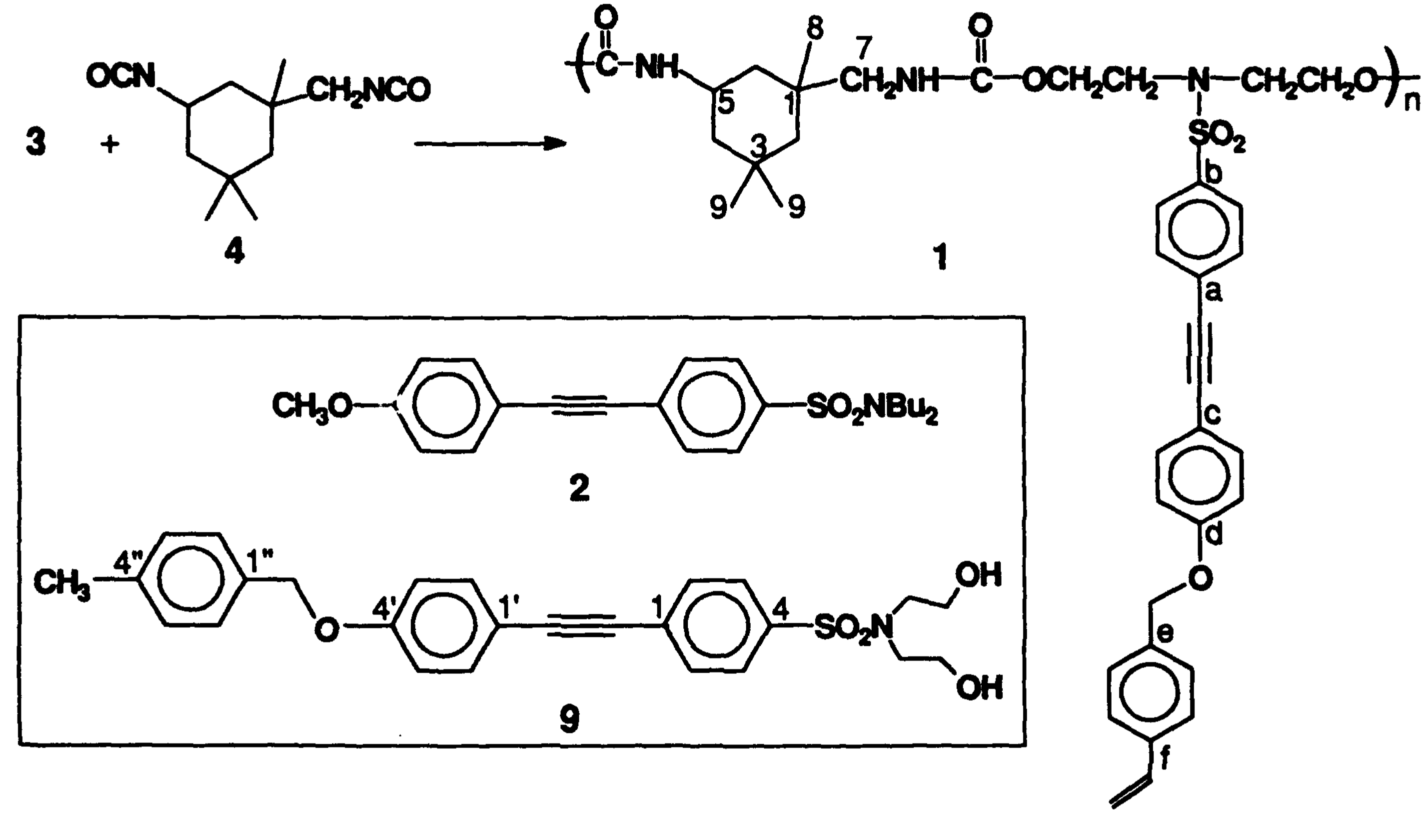
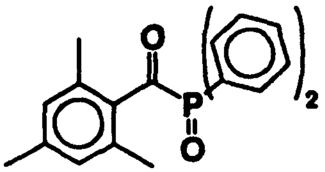
FIGURE CAPTIONS

Figure 1 UV-VIS spectra (THF) of (a) polymer **1**, (b) diol **3**, (c) chromophore model **2**, (d) compound **9**.

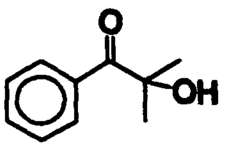
Figure 2 SH intensity decay for polymer **1** (a) before irradiation, poled at 130 °C; (b) after irradiation and poling at 130 °C; (c) after irradiation and poling at 150 °C; (d) after irradiation and poling at 170 °C; (e) after thermal crosslinking at 209 °C.



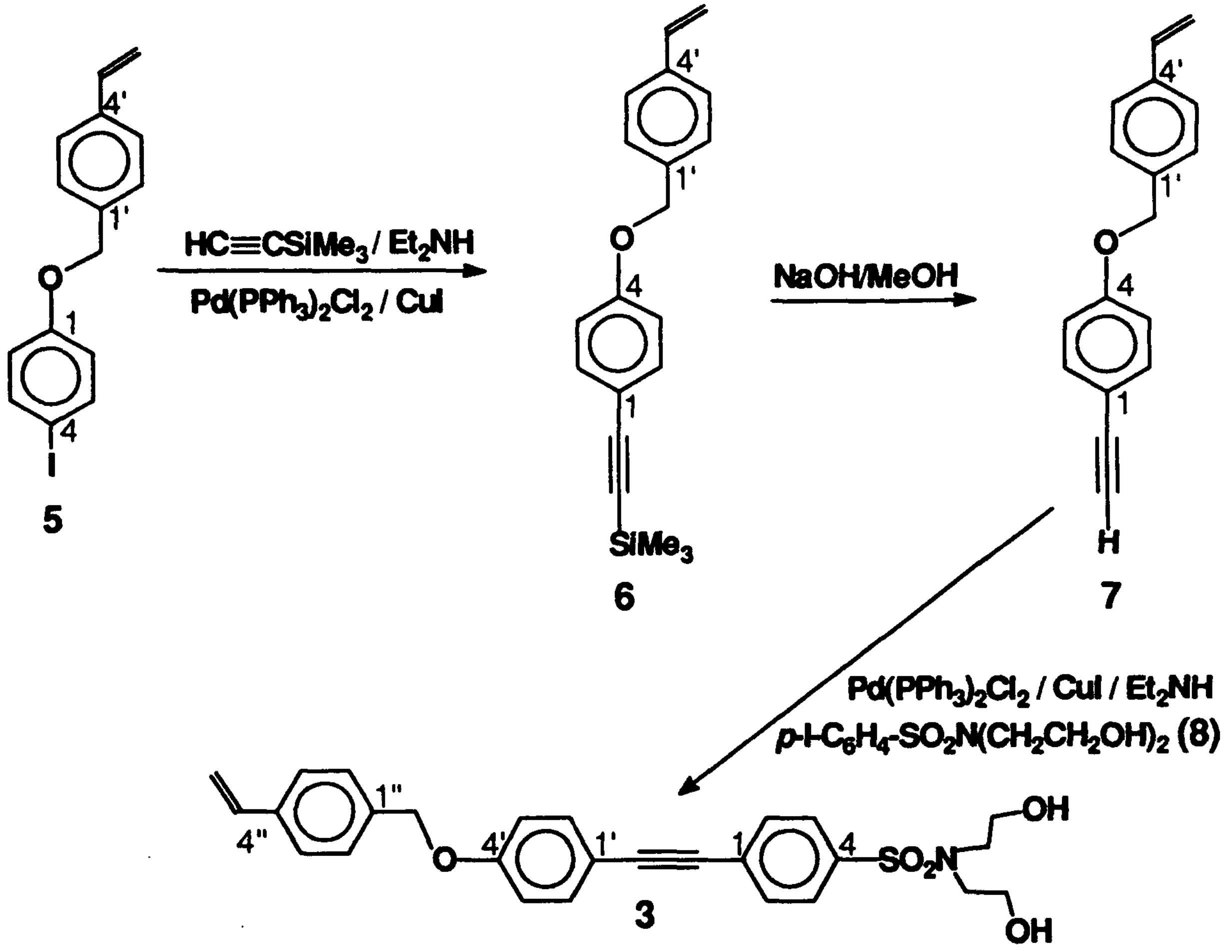
SCHEME 1



10



11


HC≡CSiMe3 / Et2NH
Pd(PPh3)2Cl2 / CuI
NaOH/MeOH
Pd(PPh3)2Cl2 / CuI / Et2NH
p-I-C6H4-SO2N(CH2CH2OH)2 (8)
4'
1'
1
4
I
5
SiMe3
6
H
7
4"
1"
O
SO2N
OH
3

SCHEME 2

FIGURE 1

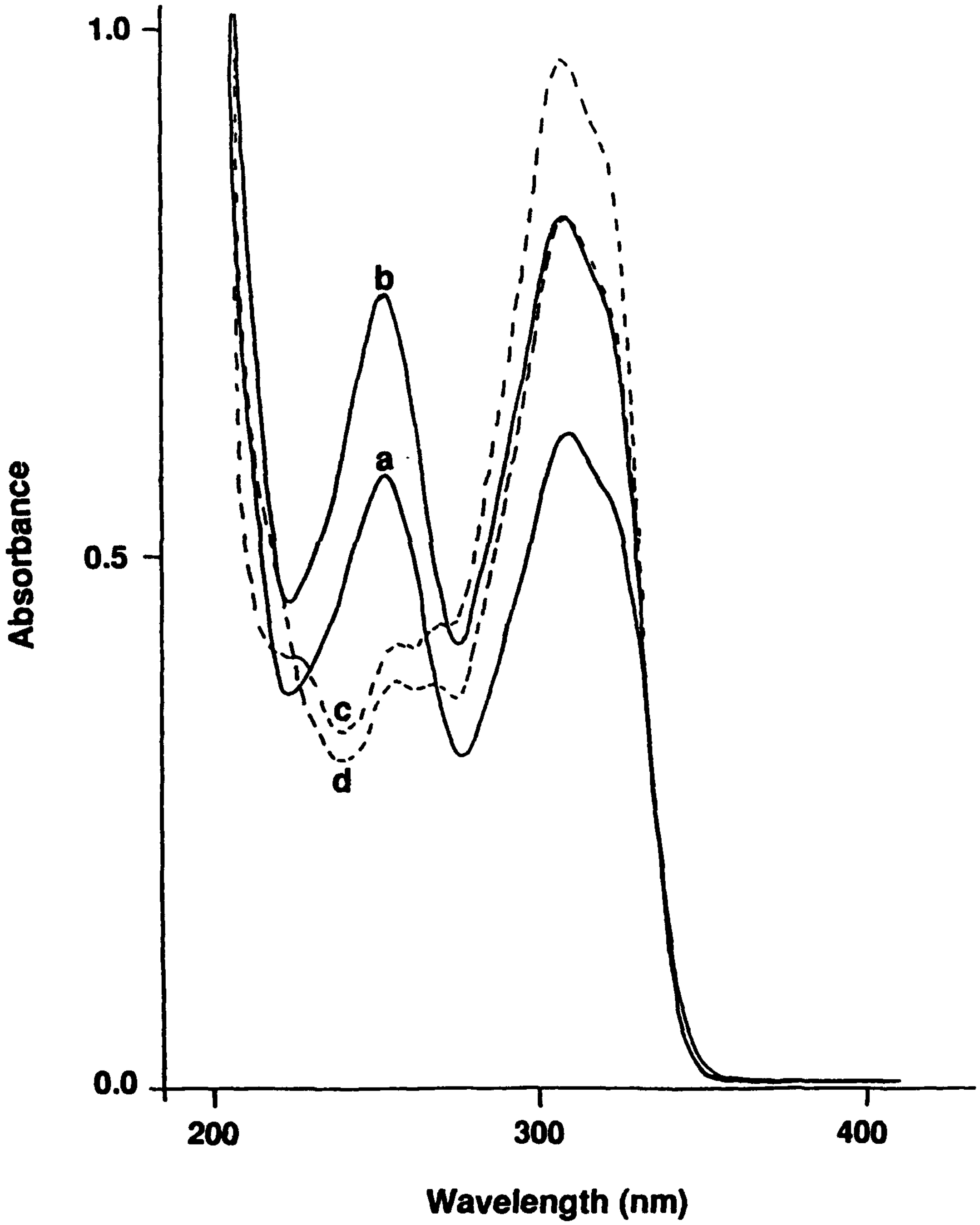
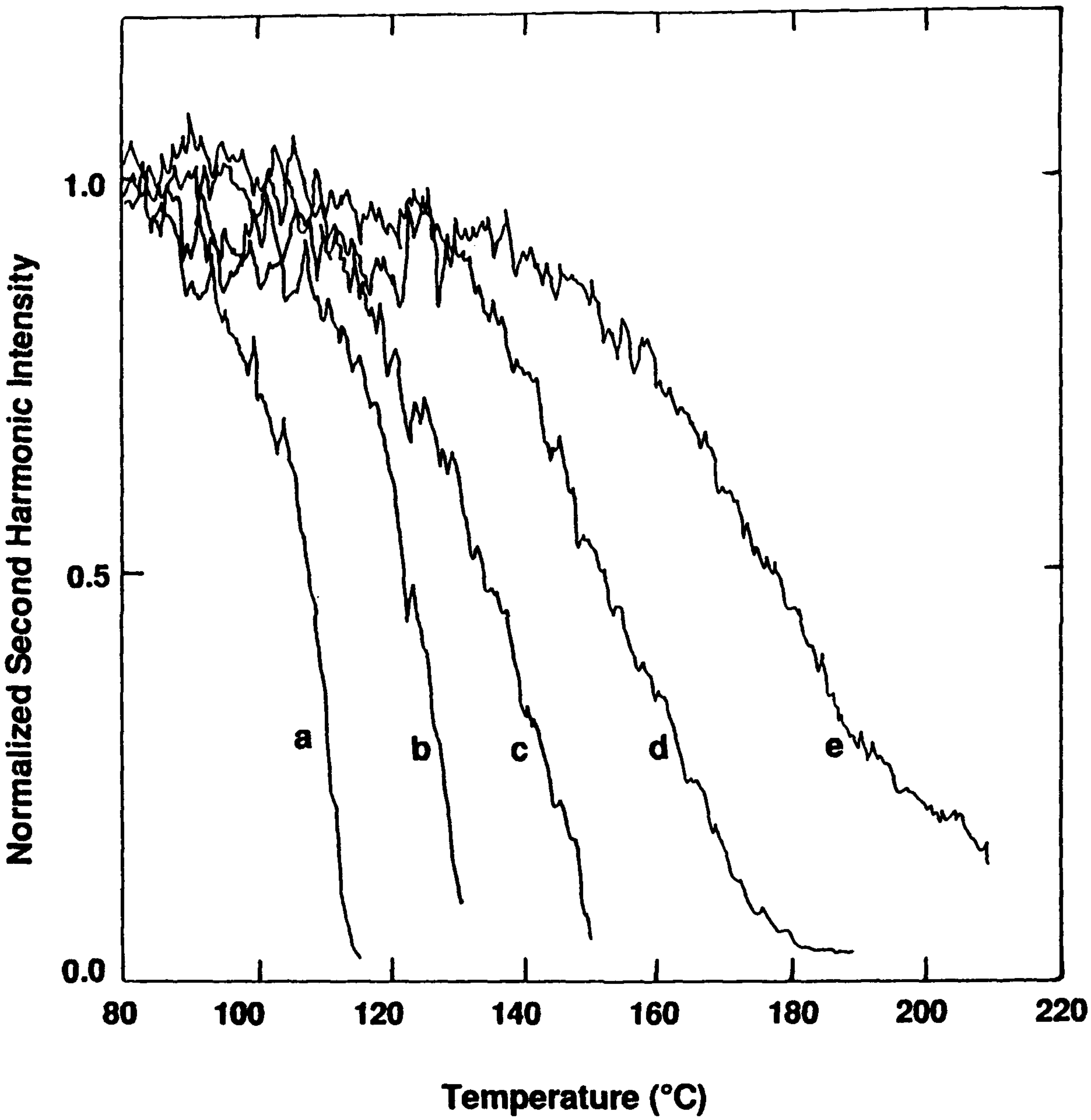


FIGURE 2


1.0
0.5
0.0
80
100
120
140
160
180
200
220
a
b
c
d
e
Normalized Second Harmonic Intensity
Temperature (°C)

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Photocrosslinking of a Polyurethane with Pendant Methacrylyl-Terminated 4-Alkoxy-4'-Sulfamoylstilbene NLO Chromophores

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13. ABSTRACT *(Maximum 200 words)*

The photocrosslinking 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-crosslinking 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 photocrosslinking 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.

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Photocrosslinking of a polyurethane with pendant methacryloyl-terminated 4-alkoxy-4'-sulfamoylstilbene NLO chromophores

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Abstract.

The photocrosslinking 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-crosslinking 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 photocrosslinking 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 then "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 crosslinking 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 crosslinking[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 photo-induced crosslinking via either a [2+2]cycloaddition of cinnamates,[11-13] a photo-activated reaction of benzophenone with butenyl side groups,[14] or a photo-cleavage 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-crosslinked systems and thermally crosslinked materials, is pattern delineation. Photo-crosslinking is inherently position-dependent by virtue of the fact that one can readily target specific areas of the sample for crosslinking 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-crosslinking 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 crosslinking to stabilize the anisotropic alignment of the chromophores and to concurrently photo-image 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 crosslinkable polymrer that contains a pendant sulfonamide chromophore.[18] In this paper, we discuss the synthesis and characterization of a photocrosslinkable polyurethane with NLO side chains, and the results from photo-crosslinking and electrooptic stability studies.

Results and Discussion.

Our design for photo-patternable NLO polymers is based on polymers containing reactive pendant groups that can be crosslinked using a photoinitiated radical process (Scheme 1). Polyurethane **1** has active side chains consisting of the NLO chromophore with a crosslinkable 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 crosslinkable group. Based on its relatively high NLO activity, low λ_{max} and ease of synthesis, the 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 crosslinking.

Synthesis.

Bifunctional monomer **2** was synthesized by the *Heck* reaction[19] as outlined in Scheme 2. Aryl bromide **3** was coupled with *t*-BOC-styrene in the presence of triethylamine and catalytic amounts of palladium diacetate and tri-*o*-tolyl phosphine. 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-isocyanato-methyl-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=5,000, M_w=7,700.

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, crosslinked network through a photo-induced 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 crosslink 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 crosslinking reaction of polymer **1**. These photoinitiators (Chart 1) included 2,4,6-trimethylbenzoyldiphenyl phosphinoxide (**5**),[22, 23] 2-methoxy-2-phenyl-acetophenone (**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-cylcopentadien-1-yl)bis[2,6-difluro-3-(1H-pyrrol-1-yl)phenyl]titanium (**9**).[23] The efficiency of the photoinitiators in the solid state crosslinking 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 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 (~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 (~8%) in the absorption band at 334 nm and a slight increase (~4%) in the absorption band at 242 nm. 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 crosslinking 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 (~25%) in the C=C stretching frequency of the methacrylate double bond and only a slight decrease (~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 crosslink density, as revealed by a large decrease in the methacrylate double bond region (~40%). However, this irradiation dose also causes a ~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 (~19%) and the lower energy band at 242 nm (~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 hours 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 chromophores, it is important that no thermal crosslinking reaction occurs under the conditions used for the poling and photo-crosslinking steps. We have previously shown[17] that some thermal crosslinking 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-pro-panediyl:3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate (Irganox 1010). Therefore, using standard photolithographic techniques in combination with this thermal inhibitor, the crosslinking 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 isopropanol:chloroform (1:1 v/v). The scanning electron micrograph of the resulting image is shown in Figure 5.

The photo-crosslinking 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-crosslinking step repeated several times on a poled sample, with the final processing step involving a flood exposure to fully crosslink the film in the absence of the electric field.

Electrooptic experiments.

The effect of the crosslinking 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 crosslinked 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 uncrosslinked 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 crosslinking 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 crosslinked without significantly affecting the NLO chromophores. In addition, we have successfully demonstrated simple photo-imaging capabilities of our NLO polymer. Micron 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-crosslinked 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 crosslinking 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 crosslinking 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 minutes 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 x 2.5 cm) were dipped halfway into hydroiodic acid (55 % in water; 50 °C), for 30s 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 @ 1kHz) was applied to the electrodes. Linearly-polarized light (1 mW, 633n, 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 mm Hg and 0 °C/10 mm Hg, respectively). 3-bromopropyl methacrylate was made according to literature[27] and purified by distillation (46-52 °C/0.25 mm Hg). 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 chromotography. ^1H 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 Hz. 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 μ Hewlett Packard columns (330 x 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 Corporation 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-bromophenylsulfonamide (3)

A solution of 4-bromobenzenesulfonyl chloride (5.01 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 CHCl3 gave 5.25 g (83%) of colorless **3**: mp 99-101 °C; ^1H 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)sulphamoyl]stilbene (4)

A mixture of **3** (3.00 g, 9.25 mmol), 4-(t-butoxycarbonyloxy)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 CHCl3, 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-Methacryloylpropyloxy)-4'-[N,N-bis(2-hydroxyethyl)sulphamoyl]-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-bromopropylmethacrylate (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 12h of stirring at rt, water was added and the precipitate was filtered off. Flash chromatography (CHCl3/MeOH 10:1 v/v), followed by recrystallization (CHCl3/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_2-C*H*$_2$-CH_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=C*H*), 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 diethylether and hexanes: yield: 3.28 g (61%) 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=C-C*H*$_3$), 2.07 (br s, 2H, CH_2C*H*$_2$$CH_2$), 2.70 (br s, 2H, C*H*$_2$NH), 3.35 (br. s, 4H, NC*H*$_2$$CH_2$O), 3.47, 3.49 (2 s, together 1H, C*H*NH), 3.55 (br s, 2H, NH) 4.06 (br. s, 6H, C*H*$_2$OPh and NCH_2C*H*$_2$O), 4.24 (s, 2H, COOC*H*$_2$$CH_2$$CH_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, 45.4, 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. Cacld 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.

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Figure Captions

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.

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).

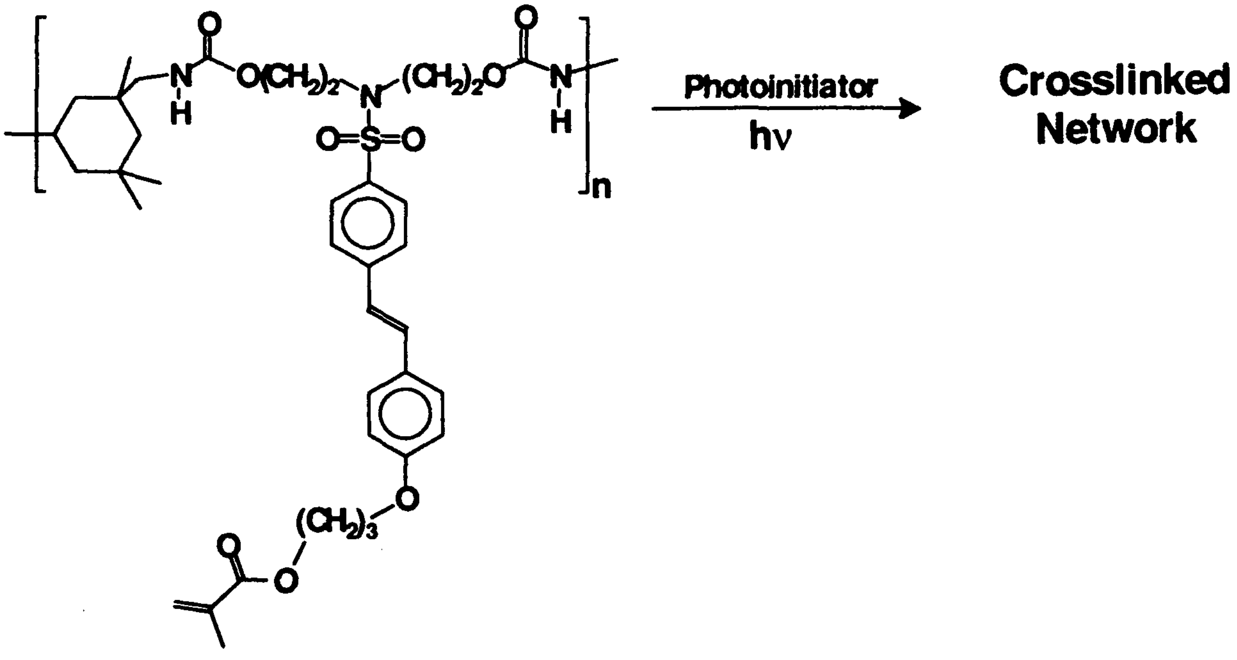
Figure 3 Change in infrared C=O and C=C absorptions of polyurethane film containing 10 wt % **9** with increasing radiation dose (532 nm, 150 °C). (a) Prior to irradiation; with irradiation of (b) 1.2, (c) 3.2 J/cm^2.

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).

Figure 5 Scanning electron micrograph of negative tone image.

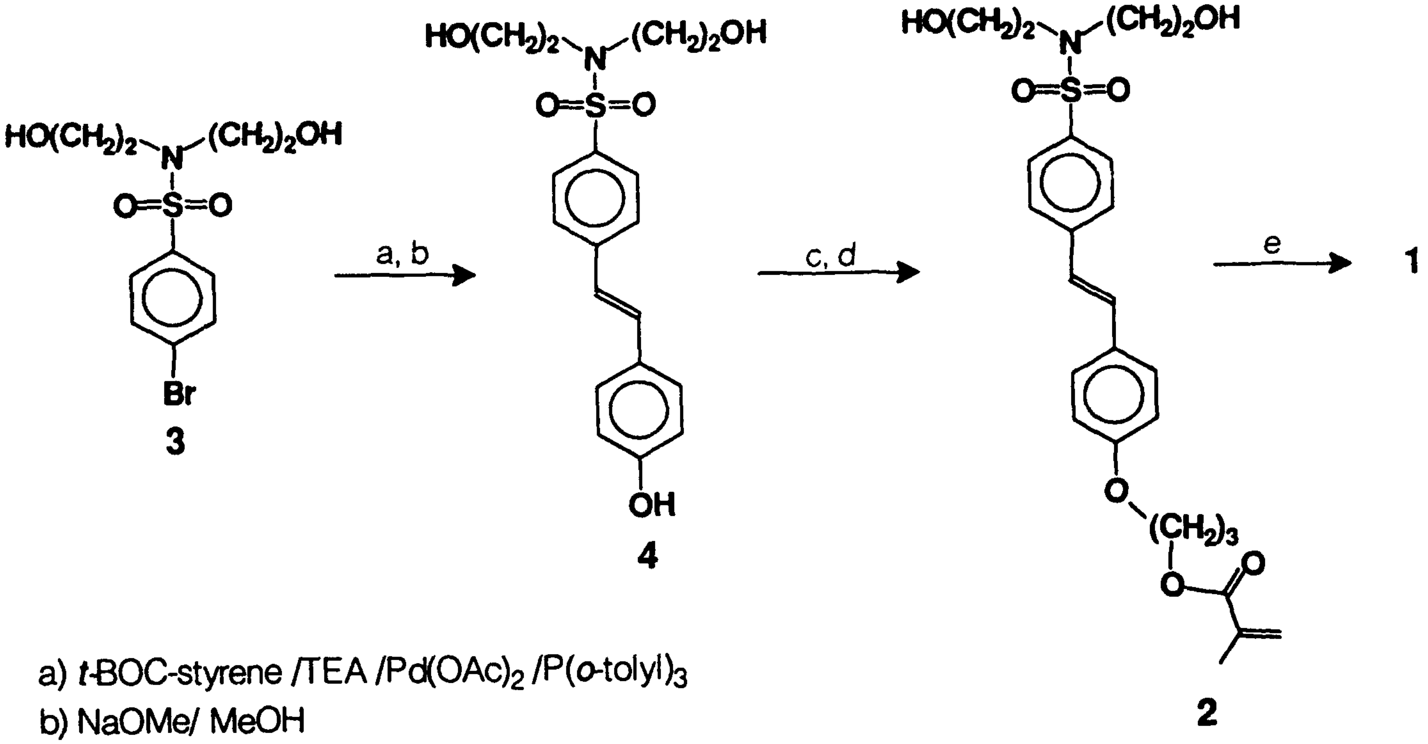
Figure 6 Normalized electrooptic signal as a function of time at 100 °C.

Scheme 1


O
O(CH2)2
N
(CH2)2O
O
N
H
N
H
O=S=O
n
(CH2)3
O
O
O
Photoinitiator
hν
Crosslinked
Network

1

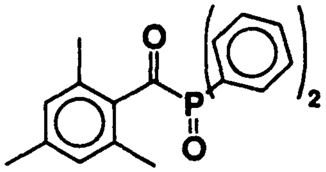
Scheme 2



a) *t*-BOC-styrene /TEA /Pd(OAc)$_2$ /P(*o*-tolyl)$_3$
b) NaOMe/ MeOH
c) NaOH
d) 3-bromopropylmethacrylate
e) isophoronediisocyanate / DABCO

Chart 1

Photoinitiators:



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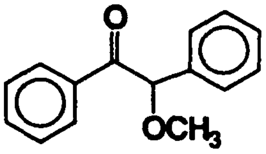
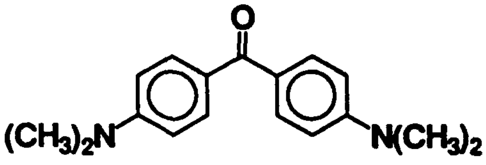
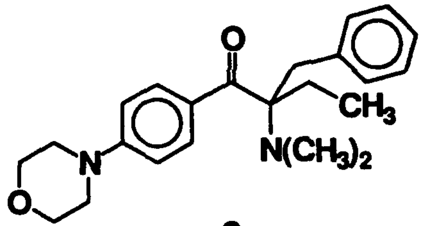


+



6

7



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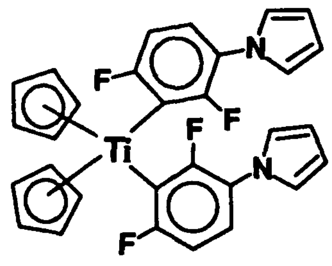

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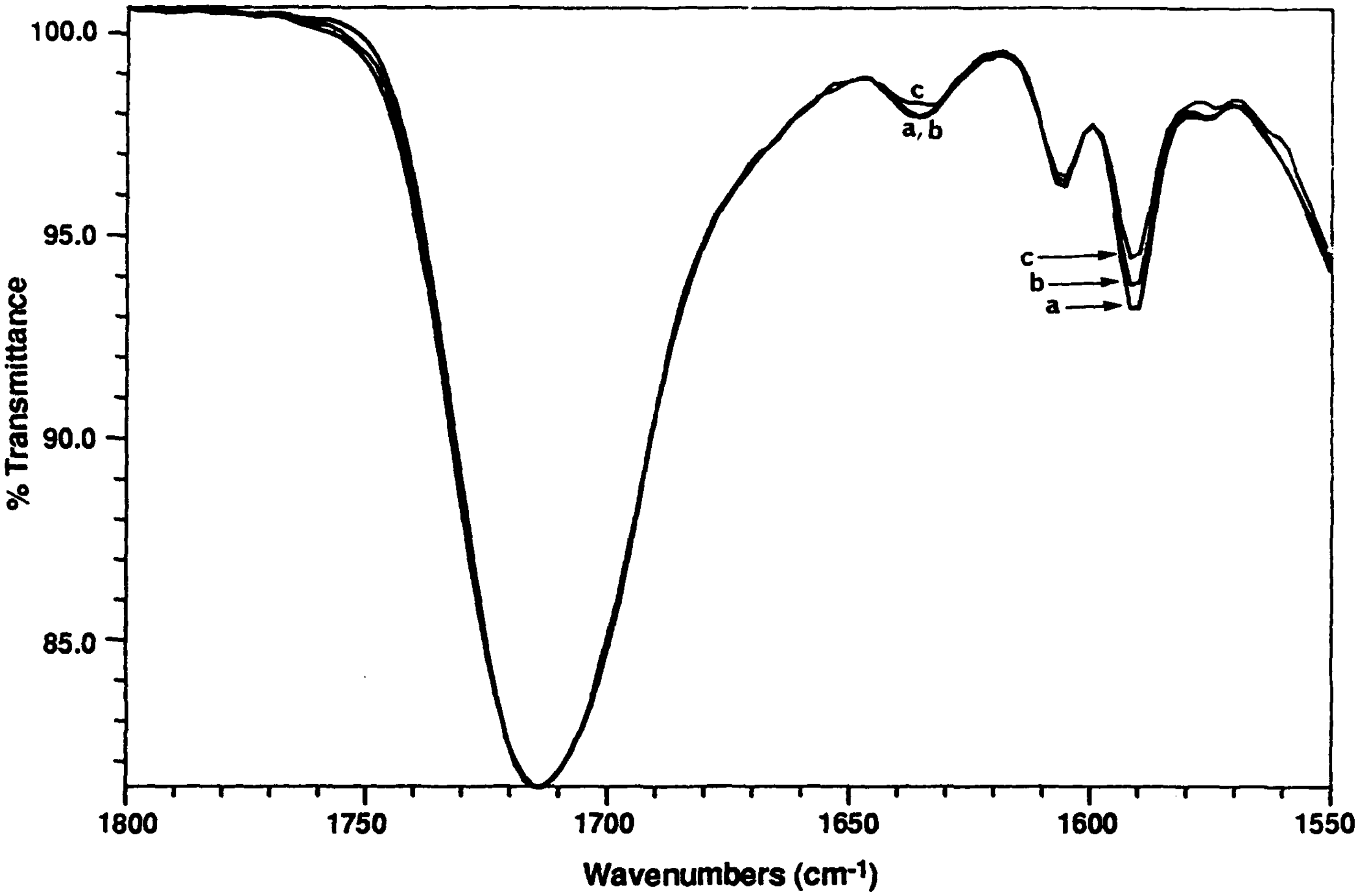
100.0
95.0
90.0
85.0
% Transmittance
1800
1750
1700
1650
1600
1550
Wavenumbers (cm^{-1})
c
a, b
c
b
a

Figure 1

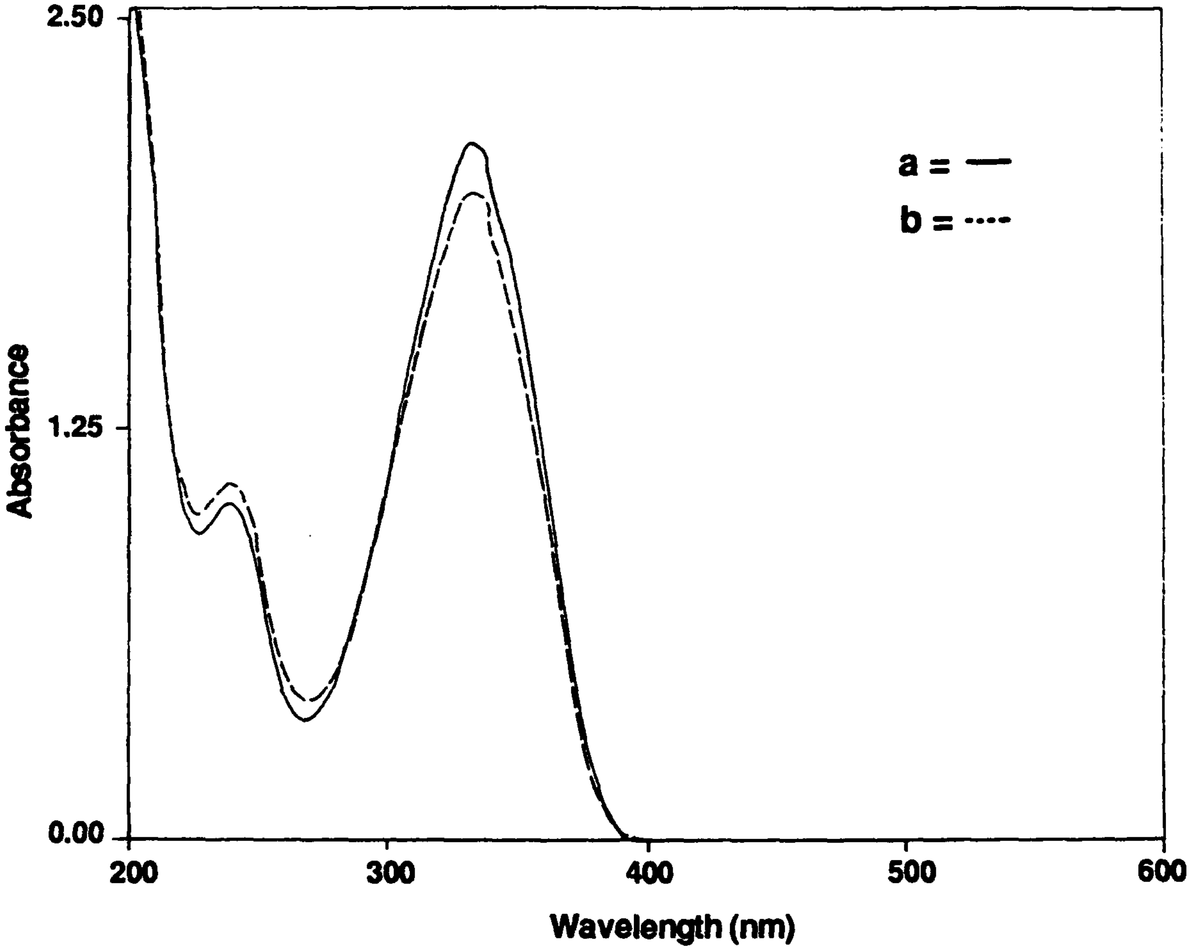

Figure 2

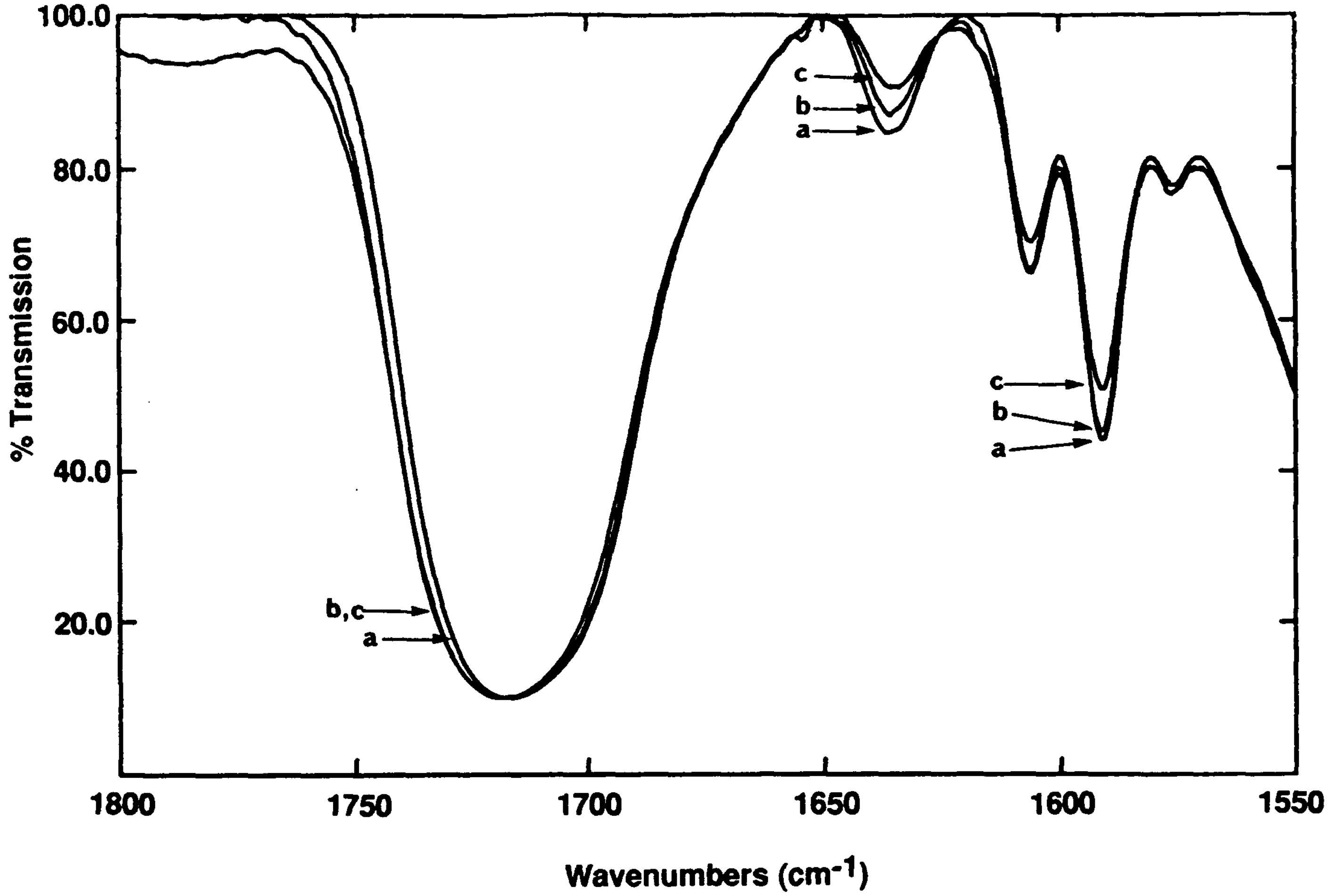
100.0
80.0
60.0
40.0
20.0
% Transmission
1800
1750
1700
1650
1600
1550
Wavenumbers (cm^{-1})
c
b
a
c
b
a
b,c
a

Figure 3

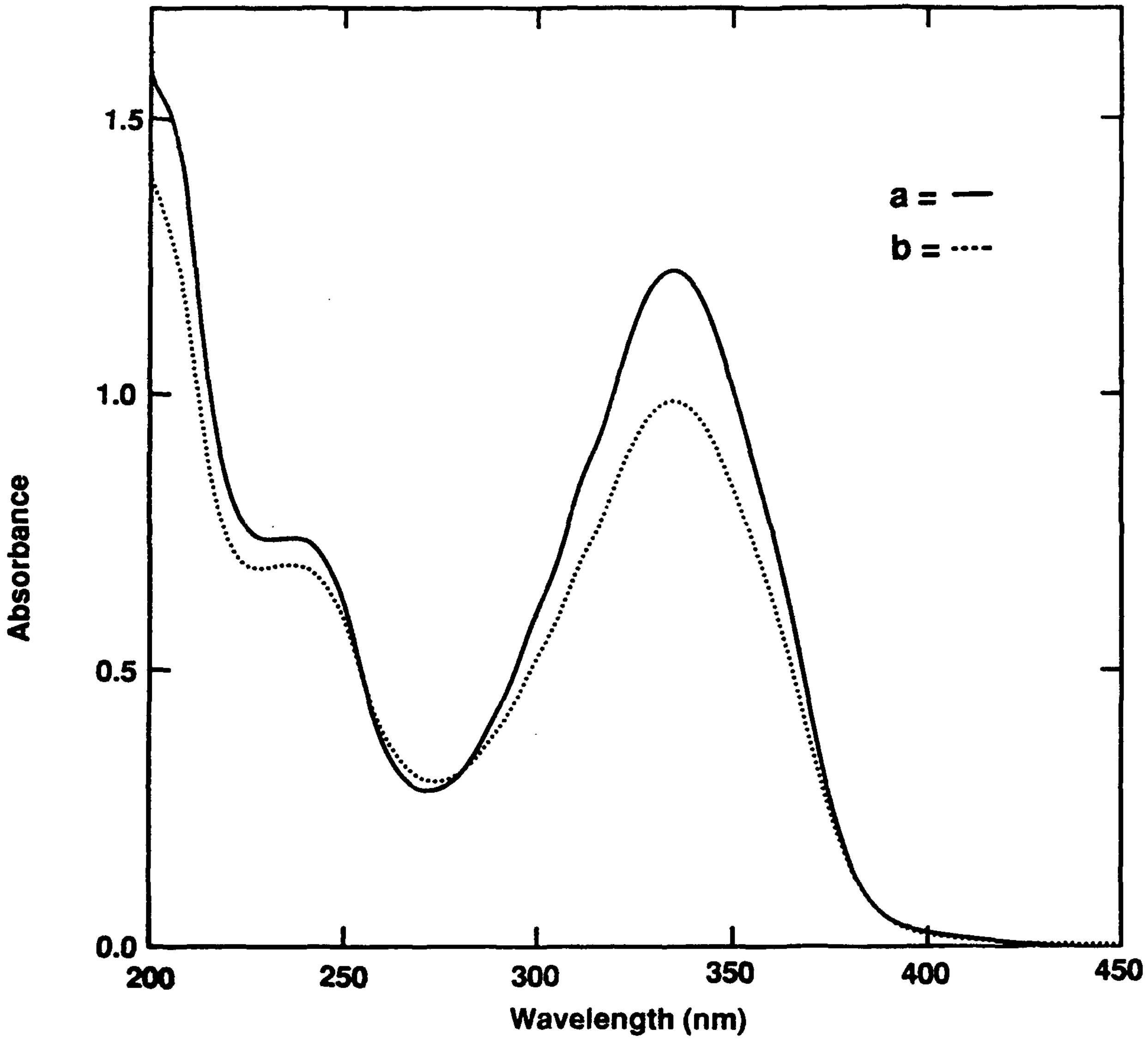
Absorbance
0.0
0.5
1.0
1.5
200
250
300
350
400
450
Wavelength (nm)
a = —
b = ····

Figure 4

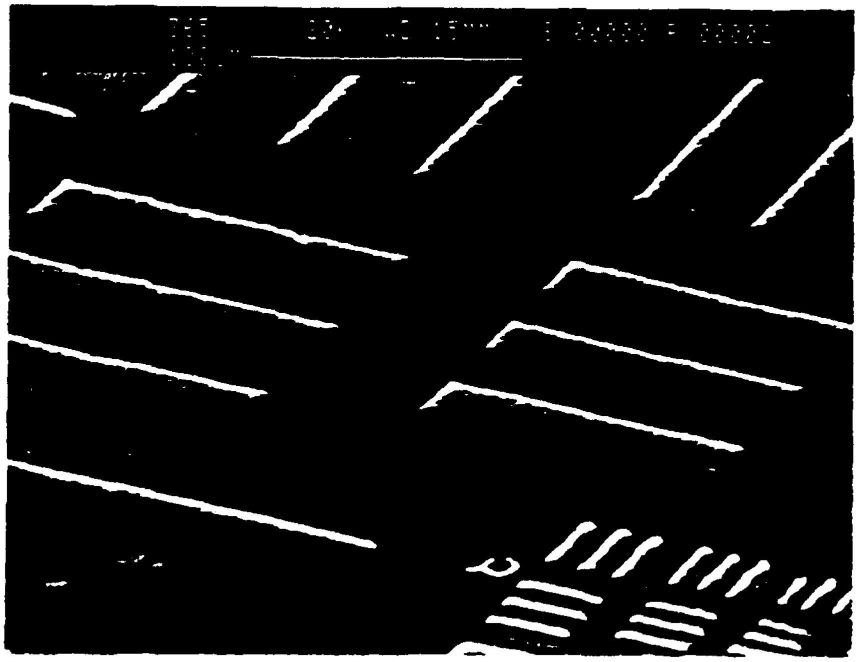

Figure 5

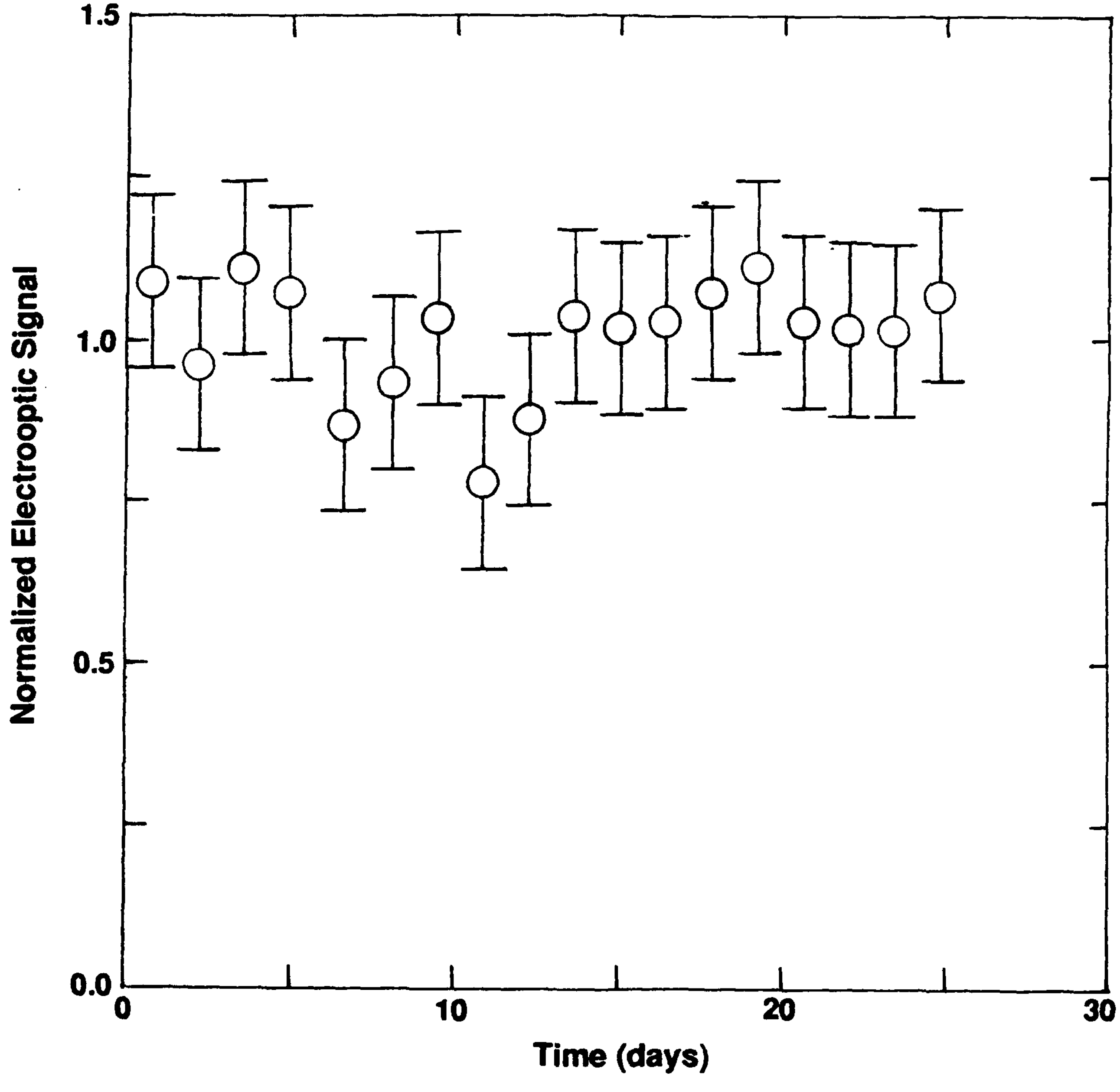
1.5
1.0
0.5
0.0
Normalized Electrooptic Signal
0
10
20
30
Time (days)

Figure 6

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Dr. Kenneth J. Wynne

Technical Report #17

Photogenerated Base in Polymer Curing & Imaging: Radiation-Induced Crosslinking via a Knoevenagel Reaction

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April 26, 1994

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13. ABSTRACT *(Maximum 200 words)*

The use of amine catalysts generated *in situ* within a polymer film to its effect insolubilization is explored. The design of the polymer includes reactive pendant group that can react with the photogenerated amine to afford stabilized enolate anions. These enolates can then be used in addition reactions such as the Knoevenagel reaction that result in the formation of new carbon-carbon bonds with concomitant crosslinking of the polymer. Copolymers of methyl methacrylate and 2-acetoacetoxyethyl methacrylate (AAEM). The copolymers containing a sufficient proportion of AAEM are highly soluble in a variety of solvents including aqueous base. Crosslinking of films of the copolymers containing a photobase generator such as [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine and an acceptor molecule such as a dialdehyde can be achieved by exposure to UV light at 280 nm. The resist sensitivity achieved is high reaching *ca.* 40 mJ/cm^2. Photocrosslinking and imaging can also be achieved in the absence of the added acceptor moiety.

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PHOTOGENERATED BASE IN POLYMER CURING & IMAGING: RADIATION-INDUCED CROSSLINKING VIA A KNOEVENAGEL REACTION.

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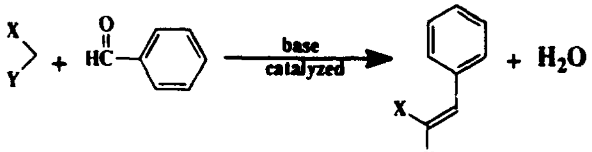
Cornell University, Ithaca, NY 14853-1301

The development of new photoactive compounds[1-3] that can liberate amine and other bases by irradiation has opened a new avenue for the development of new radiation-curable coatings, resists and imaging materials[4].

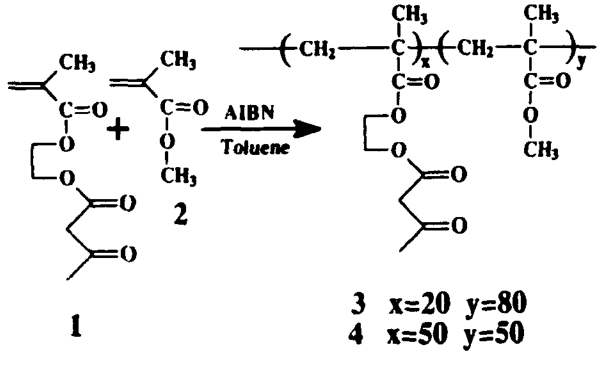
For example photogenerated base has been used in image reversal processes for a now classical type of chemically amplified resist material[5,6]. Photogenerated base has also been used in the development of imageable polyimides[7] because amines generated *in situ* within a poly(amic ester)[8] can catalyze[9] the thermal imidization process. Although numerous applications can be envisioned for photogenerated bases, for example in the crosslinking of epoxy resins, or the curing of polyurethanes, we have concentrated our efforts on the development of *imaging and resist materials* that involve base-catalyzed processes. Therefore, a new chemically amplified resist that involves the use of photogenerated base to effect the decarboxylation of a polymer side-chain has been described recently[10,11].

A number of organic reactions such as the Michael addition, the Knoevenagel reaction, etc., are known to proceed under base catalysis. This report describes the use of photogenerated base in the crosslinking of a functional polymer that contains easily enolized pendant groups. The key reaction for this crosslinking process is the base catalyzed Knoevenagel reaction that proceeds with the formation of a new carbon-carbon bond as shown below.

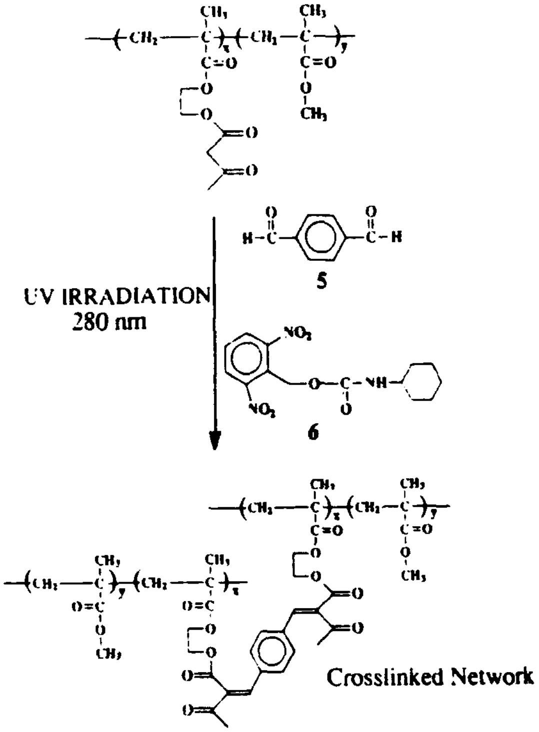


X, Y = CO_2R, C=O, CN, SO_2, NO_2, etc.

The functional polymer used for this study is obtained by polymerization of 2-acetoacetoxyethyl methacrylate (1, AAEM) or by its copolymerization with varying amounts of a comonomer such as methyl methacrylate 2. The copolymers exhibit good solubility in a variety of solvents such as acetone, tetrahydrofuran, chloroform, and diglyme, allowing for both spin-coating and solvent development after imaging.



For the imaging experiments described below, two copolymers 3 and 4 containing 20 and 50 mole% of monomer 1, respectively, as well as methyl methacrylate (80 and 50 mole%) were prepared. Resist solutions were prepared in diglyme using the copolymer, terephthalaldehyde used as a crosslinking additive, and the photoactive carbamate, [[(2,6-dinitrobenzyl)-oxy]carbonyl]cyclohexylamine, that liberates cyclohexylamine upon irradiation. It should be emphasized that a number of other polyfunctional crosslinkers susceptible to Michael, Knoevenagel, or similar reactions, are also available. An alternate mode of crosslinking has also been achieved using the copolymer and the photobase generator alone. The overall crosslinking process in the presence of a bifunctional receptor molecule is shown schematically below.



Upon irradiation of a film of the copolymer, the photoactive carbamate is photolyzed liberating the free amine dispersed within the exposed areas of the polymer film. This latent image is then heated to 110°C to drive the crosslinking reaction, and the image is developed using an appropriate solvent to remove the unexposed areas of the resist film.

Copolymer 4 containing 50 mole% AAEM is soluble in aqueous base allowing the development step to be carried out in classical developers such as tetramethylammonium hydroxide. In contrast, the AAEM content in copolymer 3 is insufficient for image development in aqueous base and the development step can be carried out in acetone.

Exposure experiments, using a multidensity mask that provides for different exposure doses to be transmitted to different areas of the resist film in a single operation, were used to determine the sensitivity of the resist. The sensitivity curve shown in Figure 1 confirms that the resist has a high sensitivity (near 40 mJ/cm^2 for exposure at 280 nm) but does not appear to be chemically amplified. Several design modifications are currently under investigation to achieve chemical amplification in a truly photocatalytic system.

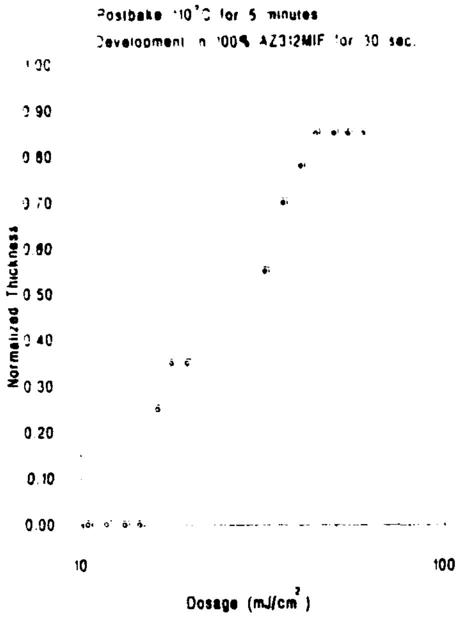


Figure 1. Sensitivity curve for a resist derived from 4

Although FT-IR monitoring of the reaction failed to provide conclusive information on the crosslinking process, the change in UV absorption resulting from the imaging experiments supports the formation of a conjugated system as a result of Knoevenagel reaction of the polymer with the dialdehyde. Therefore, Figure 2 shows the UV absorbance of a resist film before (Fig. 2a) and after (Fig. 2b) exposure to a high dose of UV radiation (ca. 300 mJ/cm^2 at 280nm) and post-baking at 130 °C for 5 minutes.

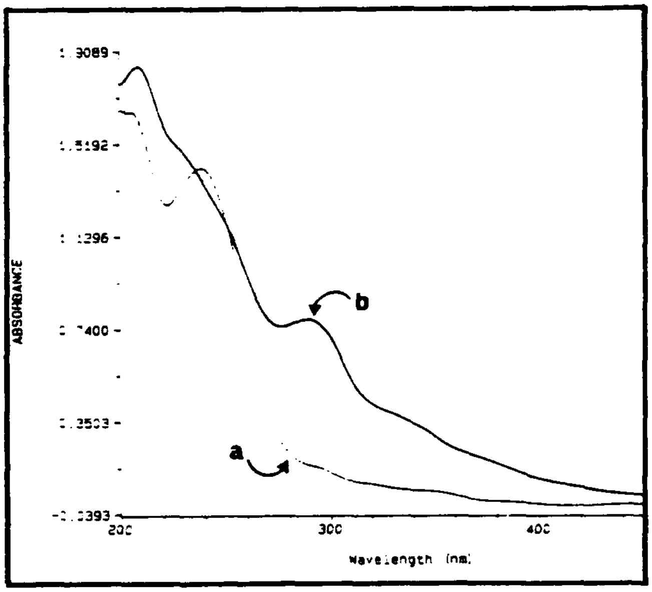


Figure 2. UV spectrum of the resist before (a) and after (b) exposure to deep-UV radiation at 280 nm.

Conclusion.

These experiments demonstrate that photogenerated base can be used for the curing and imaging of polymers through *in situ* formation of stabilized enolates and their subsequent reactions that lead to new C-C bonds.

Experimental Procedure

Preparation of a copolymer containing 50 mole% AAEM.

A solution of freshly distilled 2-acetoacetoxyethyl methacrylate (4.5g, 21 mmoles) and freshly distilled methyl methacrylate (2.1g, 21 mmoles) in 10 mL toluene containing AIBN (71mg, 0.43 mmole or 1 mole% with respect to monomers) was heated to 80 C for 18h. The polymer was collected and reprecipitated into methanol then dried to afford 6.5g of a glassy solid. Characterization by GPC (viscometric and RI detectors, universal calibration with polystyrene standards) gave Mn = 22,000 and Mw = 68,600. The NMR analysis of the polymer confirmed that it had the expected structure.

Imaging experiments: determination of resist sensitivity.

A resist solution was prepared from 0.245 g of the copolymer prepared above, 0.086g of terephthalaldehyde, and 0.073g of [[(2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine in 0.830g of diglyme. The filtered resist solution was spin-coated onto silicon wafers that were subsequently pre-baked at 110 °C for 3 minutes affording films 1 micrometer in thickness. Exposure at 280nm (interference filter) through a gradient multidensity mask (Ditric Optics) afforded a composite image with areas of different exposure doses. After post-baking at 110°C for 5 min, the image was developed using the aqueous base developer AZ312MIF.

Acknowledgements

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