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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] 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 NLO properties of these materials are lost. Stabilization of the poled orientation can be achieved by cross-linking the polymer either thermally[1-8] or photochemically.[9-11] An advantage of photochemical cross-linking is the ability to directly create devices using photoimaging. The [2 + 2] cycloaddition of cinnamates[10] and the photocleavage of azides to nitrenes[11] have been used, but these processes are incompatible with desirable chromophores based on stilbene or azobenzene. Our goal is to use photochemical cross-linking both to stabilize the anisotropic alignment of the chromophores and, concurrently, to photoimage the polymers for the direct fabrication of devices. An additional target is the frequency doubling of laser diode light (800–900 nm) which requires optically transparent materials at both the fundamental wavelength and the half-wavelength.

To achieve our target, monomer **1** containing two distinct polymerizable groups connected through a donor acceptor stilbene chromophore[12] has been synthesized.[13] Polymerization of **1** with isophorone diisocyanate in the presence of diazabicyclo[2.2.2]-octane affords[14] the desired colorless polyurethane **2** (Scheme I).

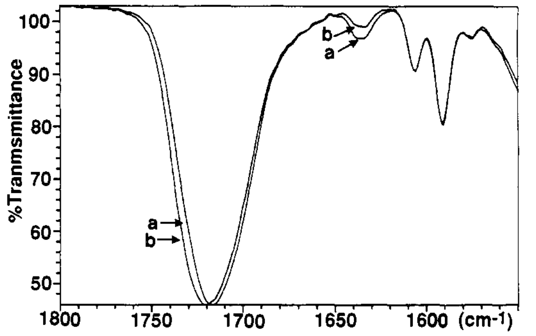
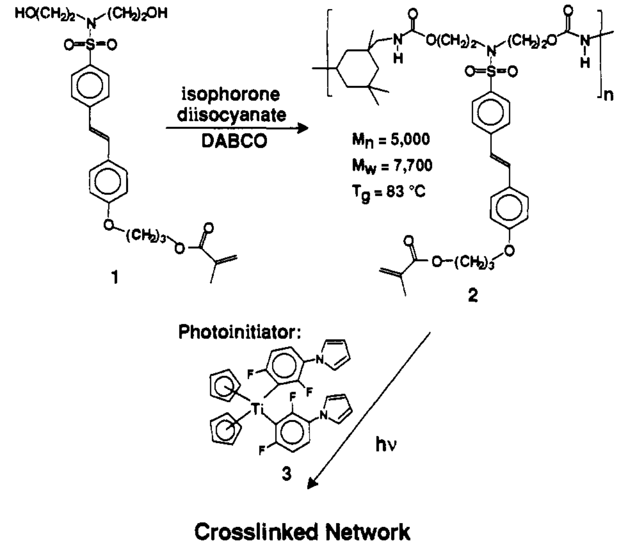


Figure 1. IR spectra for C=C region of polymer films (1 μm thick) containing 10 wt % of **3**: (a) before irradiation; (b) after irradiation at 150 °C with 350-W Hg lamp (436-nm filter, 2 J/cm²).

Scheme I



The photoinitiator used to cross-link the polymer must not cause isomerization of the stilbene by either direct or sensitized irradiation. The titanocene photoinitiator **3** meets these requirements while also bleaching upon photoreaction.[15] The photocross-linking of a film of polyurethane **2** containing 10 wt % of **3** was monitored by IR spectroscopy (Figure 1). The methacrylate C=C stretching frequency at 1636 cm^{-1} decreased upon exposure to light, while the *trans*-stilbene C=C at 1590 cm^{-1} remained essentially unchanged. Additionally, a shift from 1717 cm^{-1} to 1721 cm^{-1} in the C=O 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

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[13] *N*,*N*-Bis(2-hydroxyethyl)-4-bromobenzenesulfonamide was coupled with *t*-BOC-styrene in the presence of Et_3N and catalytic amounts of Pd-$(OAc)_2$ and tri-*o*-tolylphosphine. Subsequent deprotection with NaOMe in MeOH produced 4-hydroxy-4′-[*N*,*N*-bis(2-hydroxyethyl)sulfamoyl]stilbene. Removal of the phenolic proton of the stilbene with NaOH and reaction with 3-bromopropyl methacrylate gave monomer **2** in 44% overall yield.

[14] Polymerization conditions: THF, 10 days, reflux. The polymer in THF has λ_{max} (log ε) = 242 (4.173), 332 nm (4.295).

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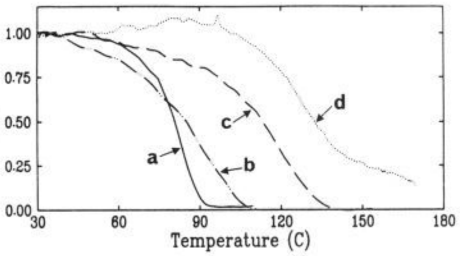

Figure 2. SH intensity decay ($\lambda_{\text{fundamental}}$ = 1064 nm) for polymer films (ca. 2.5 μm) containing 10 wt % of **3**. All samples were heated at 5 °C/min to poling temperature, electrode poled with 40 V for 5 min, cooled to 30 °C at 5 °C/min, and reheated at 3 °C/min while the SH intensity was being recorded: **(a)** sample poled at 90 °C; **(b)** sample containing 0.5 wt % of Irganox 1010 poled at 150 °C; **(c)** sample poled at 150 °C in the absence of inhibitor, **(d)** sample containing 0.5 wt % of Irganox 1010 poled at 150 °C and irradiated with a frequency-doubled CW mode-locked Nd:YAG laser (532 nm, 4 J/cm²).

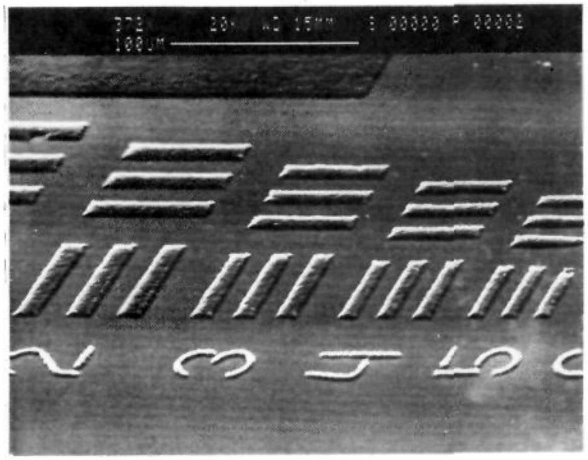

Figure 3. Scanning electron micrograph of negative-tone image.

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. For comparison purposes, we define T_{max} as the temperature at which the greatest amount of orientational relaxation is occurring, *i.e.*, the inflection point in the curve showing the loss of the SH signal.

To achieve photopatterning with concurrent stabilization of the poled chromophores, no thermal cross-linking reaction should occur under the conditions of poling and photo-cross-linking. Therefore, we have studied the relaxation of the polymer after it was poled at 90 °C and at 150 °C and after it was poled *and* irradiated at 150 °C (Figure 2).[16] Nonirradiated films that had been poled at 90 °C show a rapid decay of SH intensity (Figure 2a) upon heating above 55 °C, with T_{max} reached at 82 °C (corresponding to T_g for the un-cross-linked 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 cross-linking has occurred (Figure 2c). This thermal cross-linking reaction is essentially eliminated, even at 150 °C, by incorporating a hindered phenol, 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), into the polymer films to inhibit the formation of radicals (Figure 2b). Irradiation of polymer films, containing the photoinitiator and the inhibitor, at 150 °C raises T_{max} to 130 °C (Figure 2d). This photo-cross-linking reaction (free of competing thermal event) provides for stabilization of the orientation of the NLO chromophores and also patterning. The scanning electron micrograph[17] (Figure 3) shows an image created by irradiating the polymer at 150 °C through a mask with 5-μm features, followed by image development.

Long-term stability studies of the photo-cross-linked films poled at 150 °C show that the NLO response, measured as the electrooptic coefficient r_{33}, remains high (0.5 pm/V at 633 nm on a film 2.1 μm thick with poling at 50 V) 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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(17) Image obtained by irradiation (532 nm, 4 J/cm², 150 °C) of 2.5-μm film containing 10 wt % of **3** and 0.5 wt % of Irganox 1010 and developed in 1:1 2-propanol/chloroform (v/v). Imaging is accompanied by ca. 4% shrinkage. Wet development is not necessary in practical applications.