

Phase-matched second-harmonic generation in cross-linking polyurethane films by thermal-assisted optical poling

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Phase-matched second-harmonic generation (SHG) in thermal-cross-linking polyurethane films was demonstrated using a thermal-assisted nonresonant optical poling technique. During the seeding process, samples heated in an oven were irradiated simultaneously by coherent superposition of the 1300 nm fundamental and 650 nm second-harmonic lights of a femtosecond laser. The photoinduced second-order optical nonlinearity of the polymer films seeded at elevated temperatures kept stable at room temperature. The measurements for the dependence of SHG on the film thickness showed that a $\chi^{(2)}$ grating that satisfied the phase-matching condition for SHG was optically induced in the polymer films. © 2007 American Institute of Physics.

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Second-order nonlinear optical (NLO) polymers are very attractive for applications in optical communications and in high-density optical data storage. Poling techniques are usually used to realize the second-order NLO function of the polymer films, and all-optical poling has been demonstrated in azoaromatic acrylic copolymers using a dual frequency laser.¹⁻¹² The physical mechanism of the effect consists of two processes: orientational hole burning and reorientation of azodye molecules.⁴ Under the excitation of a fundamental light together with its second-harmonic light, orientational hole burning of azodye molecules occurs through the interference of two-photon absorption at the fundamental frequency and one-photon absorption at the doubling frequency. Orientational hole burning is followed by reverse *trans-cis-trans* isomerization, which finally leads to a net permanent polar orientation of molecules. This technique possesses some of the following advantages: phase matching for second-harmonic generation (SHG) can automatically be achieved, no electrodes are required, and micropatterning of the second-order susceptibility can be simply achieved by scanning the focal area over the sample surface.

In a resonant optical excitation process, it appears to be difficult for the SHG conversion efficiency to benefit from phase matching achieved automatically in large propagation distances due to the absorption of samples. Based on non-resonant all-optical poling using femtosecond laser pulses,⁵ phase-matched SHG with high SHG conversion efficiency can be achieved in thick films or waveguides. For the application of the poling technique to photonic devices, however, another problem to solve is to overcome the relaxation of the induced polar orientation of azodye molecules.

It is generally believed that the stability of the polar orientation of molecules can be improved by reducing the free volume.⁷ However, the decrease of the free volume will

make the light-induced polar orientation of azodye molecules very difficult. In this letter, we presented thermal-assisted optical poling, in which the thermal-cross-linking polyurethane with disperse red-19 (DR19) (prepolymer + cross-linker → cross-linking polyurethane) was used as samples. During the seeding process, polymer films heated in an oven were irradiated simultaneously by coherent superposition of the 1300 nm fundamental and 650 nm second-harmonic lights of a femtosecond laser, where both wavelengths were out of the linear absorption range of the polymer sample. The measurements for the dependence of SHG on the sample thickness showed that the SHG signals increased with the increase in thickness of the samples, indicating that a $\chi^{(2)}$ grating that satisfied the phase-matching condition for SHG was optically induced in the polymer films. The stability of the photoinduced polar orientation of the azodye molecules was improved by the thermosetting polymer matrix.

The thermal-cross-linking polyurethane consists of two kinds of monomers, as shown in Fig. 1(a). Monomer (a) is a prepolymer containing isocyanate groups and DR19, and monomer (b) is a cross-linker. Cross-linking can be thermally carried out through the chemical reaction between the hydroxyl (OH) groups of the cross-linker and the cyanate (CNO) groups of the prepolymer.⁸ The solution of the mixture [3:2 mol of monomer (a):(b)] was preheated at 80 °C for 0.5 h and then spin coated onto glass substrates. The prepolymer films were dried under vacuum for 6 h. The absorption spectrum of a 1.3 μm thick film is shown in Fig. 1(b), from which one can see that the absorption band peaks at 480 nm, and the film is almost transparent at wavelengths larger than 650 nm.

A similar experimental setup as that in Ref. 5 was used for all-optical poling of the films, in which a Ti:sapphire laser system with an optical parametric amplifier (OPA) emitted 150 fs laser pulses at a repetition rate of 1 kHz, and

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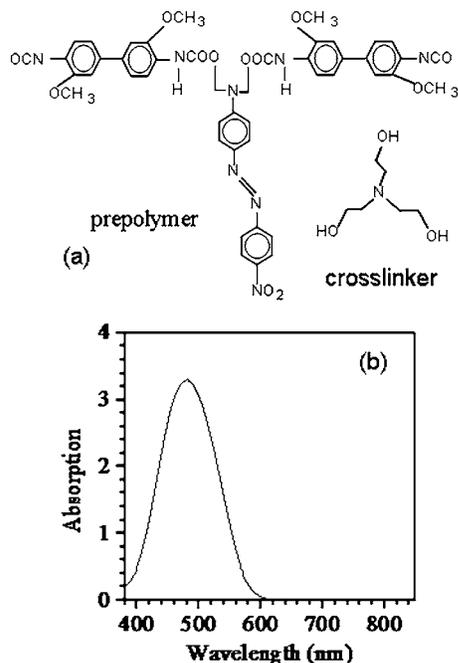


FIG. 1. Molecular structure (a) and absorption spectrum (b) of the thermal-cross-linking polyurethane with DR19. Cross-linking of the polyurethane was carried out through a thermal chemical reaction between the hydroxyl (OH) groups of the cross-linker and the cyanate (CNO) groups of the prepolymer.

the wavelength of the light from the OPA could be tuned from 300 to 3000 nm. A 1300 nm seed beam ω for all-optical poling was split from the source beam and passed through a time-delay device and a $\lambda/2$ plate to control the path length and the polarization of the beam, respectively. Another beam separated from the source beam was frequency doubled by a potassium dihydrogen phosphate crystal, which served as another seed beam, and is denoted as a seed beam 2ω here. The two collinear seed beams were introduced into the film sample through a 6 cm focal-length quartz lens. The sample was placed in an oven with windows. We achieved time superposition of pulses between the two seed beams by adjusting the time-delay device and by observing the optical Kerr effect of CS_2 . During the optical poling process, the two seed beams were introduced simultaneously into the film sample; during the probe of SHG, beam 2ω was blocked by a shutter and only beam ω remained incident. The SHG signals of beam ω were detected by a photomultiplier and observed and averaged by an oscilloscope. Beam ω passed through the sample was blocked by a heat-absorbing filter placed behind the sample and allowed only the SHG signals to pass through it. Typical fluences of the two seed beams at the sample were approximately 1.2 mJ/cm^2 for beam ω and 0.03 mJ/cm^2 for beam 2ω , respectively.

The typical decay evolution of the photoinduced SHG signals of a $15 \mu\text{m}$ azodye-doped polyurethane film (no cross-linker) seeded optically at room temperature is shown in Fig. 2(a). The seeding time was set around 10 min. The measurements on the relaxation processes were carried out at room temperature. The relaxation was mainly determined by the orientational diffusion (free volume) of the azodye molecules inside the matrix. Obviously, this relaxation will obstruct the application of the optical poling technique in photonic devices. When the thermal-cross-linking prepolymer

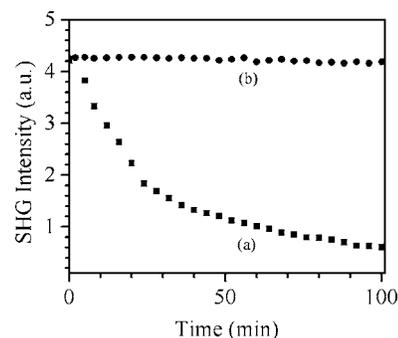


FIG. 2. Decays of the photoinduced SHG of a $15 \mu\text{m}$ azopolyurethane film (no cross-linker) (a) and a $15 \mu\text{m}$ prepolymer+cross-linker film (b), which were seeded optically at room temperature and 82°C , respectively. All measurements for SHG decays were performed at room temperature.

films were used to thermal-assisted optical poling, the hydroxyl (OH) groups of the cross-linker can react with the cyanate (CNO) groups of the prepolymer to form a three-dimensional network of polyurethane with the DR19 side groups due to the thermal excitation.¹³ This three-dimensional network can restrict the rotational motion of the azodye molecules. A $15 \mu\text{m}$ prepolymer+cross-linker film seeded optically at 82°C was cooled at room temperature, and then the decay of the induced polar orientation was measured. The seeding time was set around 10 min to make the photoinduced nonlinearity of the film to its saturation value. The SHG efficiencies for the two cases shown in Figs. 2(a) and 2(b) were measured to be about 0.1% and 0.03%, respectively. The results measured for the SHG decay of the sample are shown in Fig. 2(b). The SHG signals almost kept constant, and no tendency to further decay was found over 100 min, indicating that the stability of the photoinduced polar orientation of the azodye molecules was improved by the thermal-cross-linking polymer matrix.

In order to obtain the optimum temperature for the maximum of the photoinduced nonlinearity, we measured the dependence of optical poling on the sample temperature. The results are shown in Fig. 3. The prepolymer+cross-linker films of $15 \mu\text{m}$ thickness were maintained at different temperatures while seeding it and measuring the photoinduced SHG signals from it. The measurements were done after seeding the film and reaching the signal to its saturation value. From Fig. 3, one can find that when the temperature of the film is increased, the photoinduced SHG signals increase first, then decrease. The optimum temperature for the maxi-

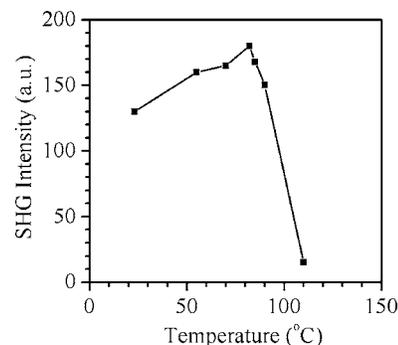


FIG. 3. Dependence of optical poling of the $15 \mu\text{m}$ prepolymer+cross-linker films on the sample temperature. The films were seeded optically at different temperatures and then cooled to room temperature to measure SHG signals.

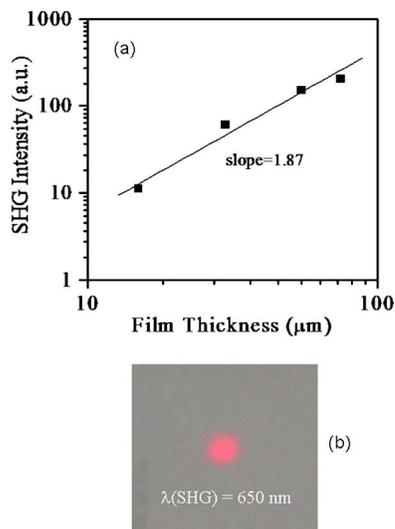


FIG. 4. (Color online) Dependence of the photoinduced SHG on the film thickness (a) and the beam pattern of the SHG signal (b). All films were seeded optically at 82 °C and then were cooled to room temperature to measure SHG signals. Log-log plots with a linear fit of a slope near 2 display SHG intensity dependence on the square of the film thickness.

imum of the light-induced nonlinearity was found to be about 82 °C. This thermal-assisted optical poling is different from the thermal-assisted electric poling, in which the sample needs to be heated above its glass transition temperature of 130 °C while applying a strong direct current electric field.

To confirm that the signals resulted from phase-matched SHG, we measured the dependence of the signal intensity versus the sample thickness. Figure 4(a) shows the results measured for the films seeded by two seed beams with wavelengths of 1300 and 650 nm, where all films were seeded optically at 82 °C and were cooled to room temperature after the photoinduced $\chi^{(2)}$ of the films increased to their saturation values. It can be seen from Fig. 4(a) that the SHG signals increase proportionally to the square of the film thickness. For a thick film with thickness of larger than SHG coherent length (the coherent length of these films was measured to be about 12 μm by using an ellipsometer), the quadratic thickness dependence of the SHG intensity occurs only in the phase-matched condition: therefore, we conclude that a $\chi^{(2)}$ grating that satisfied the phase-matching condition

for SHG was optically induced in the polymer films. Figure 4(b) shows the beam pattern of the photoinduced SHG measured for the 75 μm film, which corresponds to a SHG conversion efficiency of 0.6%. The measurements for the SHG conversion efficiency were done at a fundamental light intensity of 8 GW/cm². Obviously, this high conversion efficiency should benefit from phase-matched SHG in the thick film. It should be indicated that when 150 fs pulses are used in the azopolyurethane films, the maximum phase-matching length is estimated to be about 90 μm, which is limited by the group velocity mismatch between seed beam ω and seed beam 2ω .

In summary, we experimentally demonstrated phase-matched SHG in thermal-cross-linking polyurethane films using a thermal-assisted nonresonant optical poling technique. The second-order optical nonlinearity of the polymer films seeded at elevated temperatures kept stable at room temperature. The high SHG conversion efficiency and the quadratic dependence of SHG on film thickness showed that a $\chi^{(2)}$ grating satisfying the phase-matching condition for SHG was optically induced in the polymer films.

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