

Temperature-dependent photoinduced third-harmonic-generation variation in azo-homopolymer and azo-doped polymer thin films

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(Received 7 October 2002; accepted 19 February 2003)

The temperature effect on the variation of photoinduced third-harmonic generation (THG) of an azo-polyurethane homopolymer and an azo guest–host polymer is studied at several different temperatures. At higher temperatures, both angular hole burning and molecule angular redistribution motions weaken, due to the decreases of *cis-to-trans* thermal relaxation time and the *cis* population and the increase of orientational diffusion coefficient. Smaller photoinduced THG variation is observed in both samples at higher temperatures. Results from the THG recovery experiment show that polyurethane homopolymer thin films pumped at a high temperature have the best photoinduced THG variation stability after turning off the pump beam. © 2003 American Institute of Physics. [DOI: 10.1063/1.1568164]

Photoisomerization of azo-molecules enables easy modification of molecular linear and nonlinear polarizabilities as well as optical control of linear and nonlinear macroscopic susceptibilities, which is very important for various applications.¹ That the optical properties of azo-dye doped polymers (azo-polymer, henceforth) can be controlled optically has stimulated considerable research efforts in this direction. Todorov *et al.*² first used the *trans-cis* isomerization effect in azo-polymer thin films for holographic applications. Sekkat *et al.*³ studied photoinduced birefringence in disperse-red-1 (DR1) doped poly(methylmethacrylate) (PMMA) using attenuated total reflection method. They have shown that photoisomerization in DR1-PMMA is strongly polarization sensitive and developed a general theory of light-induced molecular angular hole burning (AHB) and angular redistribution (AR).^{4–6} The possibility of optically inducing noncentrosymmetry $\chi^{(2)}$ -susceptibility via photoassisted poling⁷ and all-optical poling⁸ has also been demonstrated. The third-order nonlinear optical phenomena related to photoisomerization have also been studied. Sekkat *et al.*^{9,10} demonstrated all-optical control of the third-order susceptibility using electric-field induced second-harmonic generation as a probing technique.

Recently, we observed large photoinduced variations of third-harmonic generation (THG) in DR1-PMMA thin films either by one- or two-photon excitation.^{11–13} The THG change observed in our previous work is attributed to the change of third-order susceptibility $\chi^{(3)}$ caused by AHB and AR of DR1 molecules.

The effect of temperature on optical poling of guest–host and side-chain polymer thin films has been reported

previously.¹⁴ It was shown there that the two polymer systems have different temperature dependences on optical poling $\chi^{(2)}$. In this work, we study the temperature dependence of the photoinduced THG change in azo-polyurethane homopolymer and azo guest–host polymer thin films. The temperature dependence of the photoinduced THG variation is of importance as it can shed light on the molecular motions associated with AHB and AR at different temperatures, and on third-order nonlinear optical properties of azo-polymer thin films.

The azo-polyurethane homopolymer thin-film samples were prepared first by dissolving the azo-polyurethane homopolymer (Tri Chemical Lab.) in cyclohexanone and then spin-coated on a pyrex glass plate.¹⁵ The remaining solvent was evaporated in a dry chamber at 90 °C for 30 min. Figure 1 shows its absorption spectrum and molecular structure. In the experiment, a Q-switched Nd:YAG laser (1064 nm, 7 ns

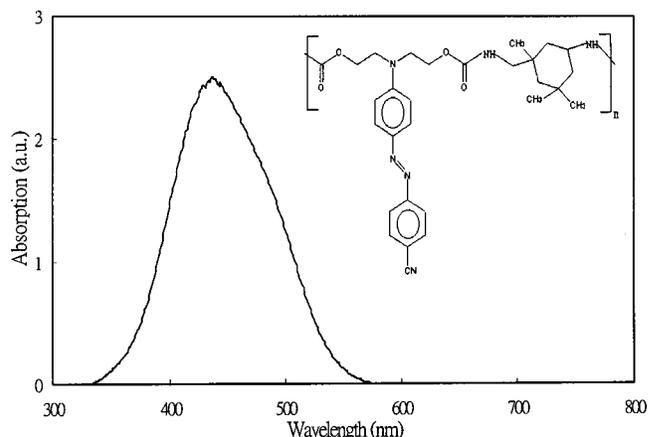


FIG. 1. Molecular structure and absorption spectrum of azo-polyurethane homopolymer.

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pulse at 10 Hz) was used as the light source. The second-harmonic (2ω) of the fundamental was used as the pump beam. A small amount of the fundamental was used as a probe to generate THG from the samples. The polarization of the pump beam was always *s* polarized; the polarization of the probe beam was arranged to be either parallel or perpendicular to that of the pump beam, forming the copolarized (\parallel) and crosspolarized (\perp) configurations, respectively. The probe beam was so weak that its pumping effect can be neglected. The average pump intensities were varied in the range of 0–0.3 W/cm² and no photobleach was observed in the thin films during the combination of irradiation and heating processes.

Figure 2 illustrates the time evolution of THG from the polyurethane homopolymer sample. Just like the photoinduced change of THG in DR1-PMMA thin films,^{14–16} the variations of THG shown in Fig. 2 arise mainly from the change of third-order susceptibility $\chi^{(3)}$. The observed THG time evolution can be interpreted as a combined effect of AHB and AR. In the three copolarized (\parallel) plots, the fast drop of THG in the first few seconds is attributed to the AHB, whereas the slow decay arises from the AR process. In the cross polarized (\perp) configuration, the AHB effect is barely detectable in the early stage of pumping, the AR effect results in a small increase of THG (see $I_{2\omega} = 12$ mW/cm²). Figure 2 clearly demonstrates the anisotropy of photoinduced change of THG in the sample. It also shows much larger decay of THG in the direction parallel to the pump polarization. This is similar to what Sekkat *et al.*¹⁶ observed in linear absorption measurements in an identical polyurethane homopolymer thin film.

Figure 3 shows the temperature effect on the decay of the photoinduced THG of the DR1-PMMA thin film in Fig. 3(a), and of the polyurethane homopolymer thin film in Fig. 3(b), for the copolarized (\parallel) configuration. In Fig. 3, time evolution of the THG signal at different temperatures are shown. Solid lines are the best fit to the data using the biexponential function

$$f(t) = A \exp(-t/\tau_A) + B \exp(-t/\tau_B) + y_0. \quad (1)$$

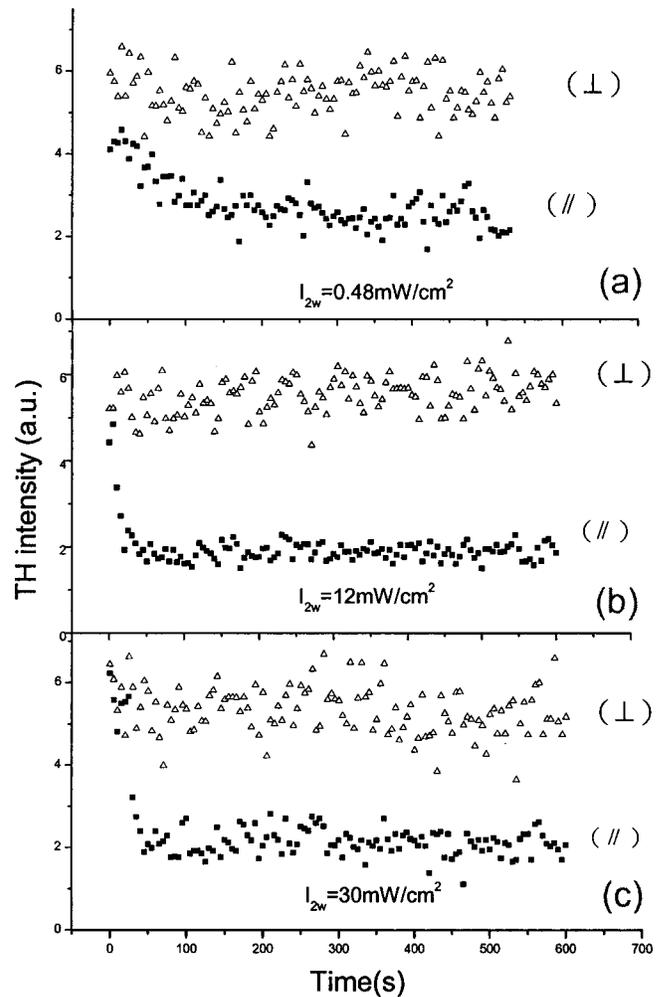


FIG. 2. Time evolution of photoinduced THG signal in the polyurethane homopolymer thin film pumped by 532 nm laser beam at three intensities. The sample was probed with the 1064 nm laser beam copolarized (\parallel) and cross polarized (\perp) with the pump beam.

The first term of Eq. (1) describes the fast THG decay caused by the AHB and the second term describes the slow THG decay caused by the AR. The best-fit parameters are shown in Table I. As shown in Table I the A and τ_A values of both

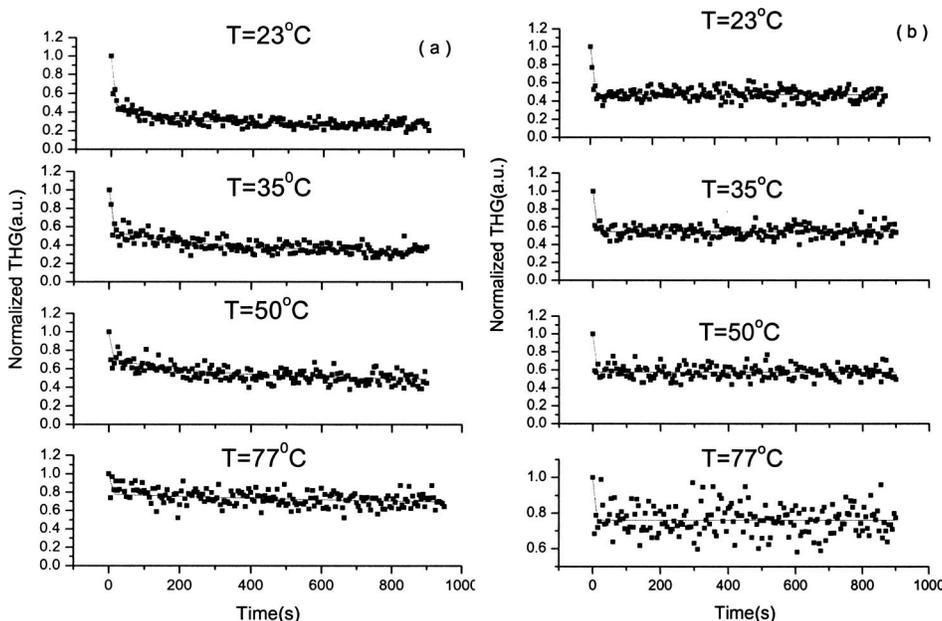


FIG. 3. Time evolutions of photoinduced THG signals from a DR1-PMMA thin film (a) and a polyurethane homopolymer thin film (b) at four different temperatures. Solid lines are the biexponential fit to the data.

TABLE I. The best parameters used in Eq. (1) to fit the THG decay data of DR1-PMMA and homopolymer films.

T ($^{\circ}\text{C}$)	DR1/PMMA					Homopolymer				
	τ_A (s)	τ_B (s)	A	B	y_0	τ_A (s)	τ_B (s)	A	B	y_0
23	5.90	163.90	0.59	0.20	0.27	6.08	2.4×10^{123}	0.54	0.12	0.36
35	5.87	269.80	0.46	0.22	0.33	2.89	3.3×10^{100}	0.45	0.03	0.51
50	0.53	300.00	0.28	0.23	0.48	1.52	5.4×10^{130}	0.42	0.01	0.56
77	0.03	1500.0	0.22	0.18	0.60	0.10	3.0×10^{149}	0.24	0.10	0.67

samples decrease when temperature increases. This arises from the decreases of the thermal relaxation time and the population of *cis* states as temperature increases. For the AR induced slow THG decay, both samples have a longer decay time constant τ_B at higher temperatures. This indicates that the AR motion is slower at higher temperatures. Recently, Sekkat *et al.*¹⁶ examined photoinduced linear absorption variations of a series of azo-polyurethane polymers, and found that the photo-orientation movement by photoisomerization of azo-dye in polymers is influenced by the polymer molecular structure, as well as by photoisomerization quantum yields and *cis-to-trans* thermal isomerization rate. They pointed out that the decrease of *cis* thermal relaxation time in azo-polymer would reduce the AHB effect and even generated a pure AR motion in one particular azo-polyurethane polymer.¹⁶ Here, we only find the decrease of the AHB effect but no increase of the AR motion when the samples are heated up. This is attributed to a larger orientational diffusion coefficient at higher temperatures. When polymers get soft, it is easier for the strong pump field to torque the molecular dipole back while the dipole is trying to reorient away from the pump field polarization. That is the reason why larger y_0 values (see Table I) appear at higher temperatures for both samples. It is also noticed that the homopolymer sample has a much longer τ_B time constant and smaller B/A coefficient ratio compared with the DR1-PMMA sample. Thus, the AR effect in the homopolymer sample is much smaller than that in the DR1-PMMA sample, due likely to the larger molecular weight of the homopolymer sample.

We also investigated the THG recovery of both samples after turning off the pump beam. Both samples were first pumped, for several minutes, with the 2ω laser beam in the copolarized (\parallel) configuration at room temperature, and at 57°C . In the latter, right after turning off the pump beam, the samples were cooled down to room temperature in 1 min and then the THG recovery was measured. The data reveal that the THG signals in the DR1-PMMA sample can be fully recovered to the original level in 2–3 min, irrespective of the temperatures at which the sample is pumped. On the other hand, the THG signals from the homopolymer samples are only partially recovered, even after waiting for 10 min. Note especially that the THG recovery is much smaller for the homopolymer sample pumped at the higher temperature. The slow THG recovery in the homopolymer sample is due likely to its large molecular weight and small free volume that re-

stricts molecular reorientation after turning off the pump. When the sample is pumped at the higher temperature, the thermal effect helps molecules to overcome some potential barriers and to stay at a more stable arrangement. Therefore, the THG recovery is much smaller in this case.

In conclusion, we have studied the photoinduced change of THG in azo-polyurethane homopolymer and DR1-PMMA thin films at several different temperatures. It is found that photoinduced THG variations in both samples are smaller at higher temperatures because of the shorter lifetime of the *cis* state and less population. Results from the THG recovery experiment show that the photoinduced THG change in the polyurethane homopolymer sample is more stable than that in the DR1-PMMA sample, consistent with its large molecular weight and small free volume. For the polyurethane homopolymer sample, increasing the pumping temperature renders the photoinduced THG change more stable.

The authors greatly acknowledge the financial supports from the National Science Council and Academia Sinica of Taiwan.

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