Intensity dependence of picosecond nonlinear response time of polydiacetylene

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(Received 10 March 1988; accepted for publication 12 September 1988)

The relaxation time of the transient degenerate four-wave mixing grating in 4-butoxycarbonylmethylurethane polydiacetylene in polymethylmethacrylate matrix films has been found to be laser energy fluence dependent. This phenomenon is attributed to a transient reversible light-induced structure change in polydiacetylene films, involving a cooperative effect originating from side-chain intramolecular hydrogen bonding.

Polydiacetylenes (PDA's) are attractive candidates for active nonlinear elements in ultrafast signal processing and optical communications because of the large and fast third-order optical nonlinearities.[1] Using optical pulses, a fast response time of PDA's was determined to be under 2 ps for resonance pumping while below 100 fs for nonresonance pumping.[2–6] The fast relaxation time was attributed to the electronic response. Recently, photoinduced irreversible structure change was observed in the blue PDA-(12,8) films.[7–9] The photochromic behavior in these blue PDA films was ascribed to the irreversible change in the bond structure in conjugated polymer backbone chains. In this letter time-resolved forward-degenerate four-wave mixing (DFWM) experiments in red form of 4-butoxycarbonylmethylurethane polydiacetylene in polymethylmethacrylate (4BCMU-PDA in PMMA) thin films using picosecond laser excitation at different incident energy fluences are reported. The decay time of the DFWM signal is found to be biexponential where the slow component is fluence dependent.

Red color films of 4BCMU-PDA in PMMA matrices were prepared from polymer solutions. After filtration of monomer solution and crystallization, the monomer crystal was irradiated for 24 h using a Ce^{137} source to obtain metallic color poly-4BCMU. Methylene chloride (MC) was used to dissolve these poly-4BCMU. After 24 h, a proper amount of PMMA was added to the PDA-MC solution. Polymer solutions were deposited to glass slides with minimum exposure to ambient atmosphere and the solidification took place in about an hour. Film samples were then sealed for laser experiments. Additional details were described elsewhere.[5]

The sample absorption was 80% at 530 nm. To avoid damaging the sample, single-shot laser pulses were used. The time between two successive shots was > 2 min. The excitation source was a mode-locked YAG laser system producing 30 ps pulses of 30 MW peak power at 530 nm. A forward DFWM geometry was used for the experiment which is displayed in the inset of Fig. 1. In this configuration, the measurement provided the information on transient grating response times. The laser pulse was split into three beams with parallel polarization. The relative time of arrival of the three incident pulses was adjustable by using two stepper-driven optical delay lines. Two pump beams ($B\,1$ and $B\,2$) separated by an angle $\theta < 5°$ were focused upon a spot about 0.5 mm in diameter on the sample such that they were both spatial and temporal coincident creating a transient grating in the medium. The grating decay was monitored by measuring the first-order diffracted light from the probe beam ($B\,3$) as a function of the delay between pump beams and the probe beam. The incident energy fluence was varied using neutral density filters.

The diffracted fourth signal beam ($B\,4$) as a function of the arrival time of the probe ($B\,3$) beam relative to the other two pump beams ($B\,1$,$B\,2$) for different energy fluences is displayed in Fig. 1. Negative time means that the probe beam arrives before the pump beams. The asymmetric profile of the signal with respect to time delay is clearly displayed in Fig. 1. The signal profile consists of a fast and a slow component. The slow component is found to be fluence dependent.

After choosing proper parameters, all the measured fluence decay profiles have been fitted by a double-exponen-

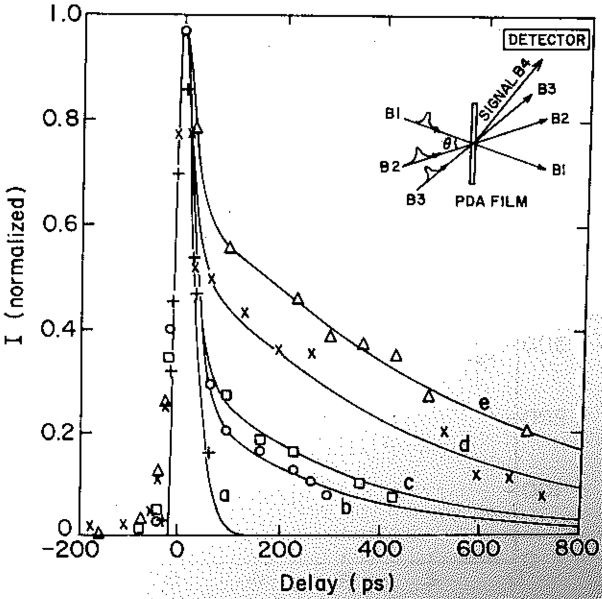

FIG. 1. Normalized DFWM signal as a function of the arrival time of $B\,3$ relative to $B\,1$ and $B\,2$ at different energy fluences (I). (a) $I < 0.50$ mJ/cm^2, $\tau_{ds} = 0$; (b) $I = 0.92$ mJ/cm^2, $\tau_{ds} = 280$ ps; (c) $I = 5.11$ mJ/cm^2, $\tau_{ds} = 320$ ps; (d) $I = 7.56$ mJ/cm^2, $\tau_{ds} = 440$ ps; (e) $I = 9.90$ mJ/cm^2, $\tau_{ds} = 600$ ps. The inset indicates the geometry of DFWM measurements.

0003-6951/88/472008-03$01.00

tial equation given by

$$I(t)\sim c(e^{-t/\tau_{df}}+re^{-t/\tau_{ds}}),\quad (t>0),\qquad (1)$$

where τ_{df} and τ_{ds} are the fast and slow components of the decay time, respectively. The data displayed in Fig. 1 can be fitted by Eq. (1) as shown by the solid lines. The rise time and the fast component of the decay slope are consistently found to be 20 ps and fluence independent.

The relationship between the slow decay time τ_{ds} and the incident fluence I is plotted in Fig. 2. The salient feature of Fig. 2 is the nonlinear dependence of τ_{ds} upon peak fluence. When the incident fluence is less than 0.50 mJ/cm^2, no obvious slow component was observed. At low fluences (0.5–5.0 mJ/cm^2), the slow component is not sensitive to increasing incident excitations. While at higher fluences, τ_{ds} increases very fast. The solid line in Fig. 2 is the calculated curve from the following equation:

$$\tau=\tau_0+a(I/I_0-1)^n,\qquad (2)$$

where $\tau_0=280$ ps, $a=0.5$ ps, $I_0=1.0$ mJ/cm^2, and n satisfies $2\leqslant n\leqslant 3$. The fitting started from $I>1.0$ mJ/cm^2. A theoretical model for the fluence dependence of τ_{ds} (I) and Eq. (2) needs to be developed.

The fast decay component is unresolved and most likely due to the electronic contributions associated with the coherent artifact.[2–5] The slow component could arise from the population grating. From photoluminescence decay measurements,[5,6] the population grating lifetime is expected to be around 12 ps. Based on our experimental results, the mechanism responsible for the slower and fluence-dependent component is probably due to photoinduced structure changes in the thin films by light irradiation. This proposed model will be discussed next.

The conjugated conformation of PDA molecular structure in the 4BCMU-PDA (in PMMA) films is stabilized by intramolecular hydrogen bondings between urethane functionalities on adjacent side chains. The conjugated length, which controls the polymer optical properties, is maintained through the cooperative effect of the array of hydrogen bondings. The reduction of conjugation length requires the simultaneous breakage of neighboring hydrogen bonds. When molecules are optically excited by the intense laser irradiation, the excess vibrational energy is dissipated internally via the strong electron-lattice interaction, leading to the breaking of H bonds. After the passage of the excitation, the structure returns to its initial state. The breakage of H bonds blocks the "pathways" for the process; therefore, the slower recovery will be associated with the larger number of the broken H bonds. The number of affected H bonds and the induced structure change are expected to depend on the laser excitation intensity due to the cooperative nature of the processes. The nonlinear rise of τ_{ds} upon the incident peak fluence implies that the number of broken H bonds and the recovery are not promoted by independent photoexcitations but through a certain cooperative multiple excitation process.

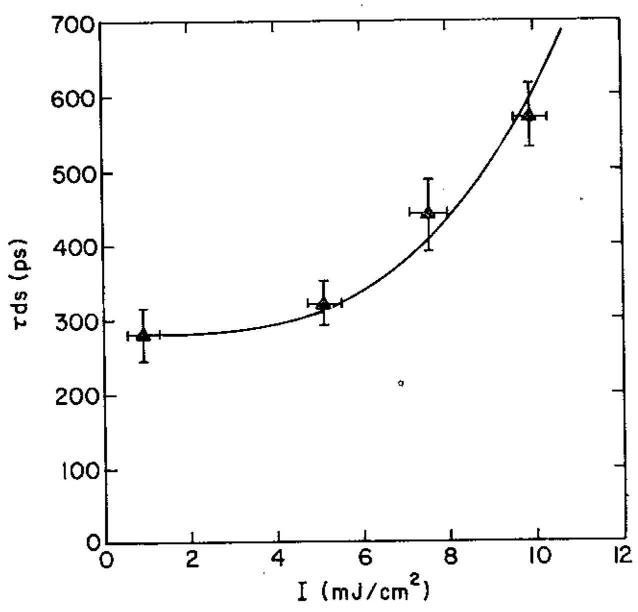

FIG. 2. Slow component of decay time τ_{ds} (ps) is a function of the incident energy fluence I (mJ/cm^2). The solid line is a curve calculated from Eq. (2), where $\tau_0=280$ ps, $a=0.5$ ps, $I_0=1.0$ mJ/cm^2, and $n=3$.

The question now is whether light-induced change is caused by heating due to high laser excitation. The expression for the laser-induced temperature rise ΔT for a semi-infinite isotropic solid, uniformly illuminated by an optical pulse of duration t_p at the surface, has been given by[10]

$$\Delta T=(1-R)\alpha E_0/\rho c,\qquad (3)$$

in the limit $t_p\ll t_0$, where R is the reflectivity of the surface (0.1), α is the absorption coefficient (2×10^3/cm), ρ is the density of PMMA (1.17 g/cm^3),[11] c is the specific heat of PMMA (1.464 J/g °C, at 23 °C),[11] and E_0 is the energy per unit area of the radiation incident on the sample (the maximum in the experiments is 10 mJ/cm^2). Substitution of the appropriate parameters into Eq. (3) yields $\Delta T(23\,^\circ\mathrm{C})=10\,^\circ\mathrm{C}$, for a single 30 ps optical pulse. The thermal response time t_0 is defined as

$$t_0=4\rho c/\pi\alpha^2K,\qquad (4)$$

where K is the thermal conductivity of PMMA (2.51×10^{-3} W/cm °C).[11] Physically, t_0 gives an order of magnitude estimate of the time for the heat to diffuse one absorption depth ($1/\alpha$). In our case, $t_0=0.22$ ms. A 110 °C temperature is needed for conformational transition by simple heating.[4] Therefore, the laser-induced temperature rise cannot affect the equilibrium of the two forms. Besides, the time response t_0 from the heating effect is 0.22 ms which is six orders of magnitude slower than τ_{ds} and six orders faster than the repetition time of the pulses. These results suggest that the heating effect is unlikely to play a significant role in this experiment.

To verify the above-proposed model, the following experiments were carried out.

Time-resolved DFWM measurement in the yellow form films was carried out. The yellow films were obtained through exposing red films to the vapor of trifluoroacetic acid (TFA), a hydrogen bond breaking agent.[12] The yellow films could be converted back to the original red films by evacuation under vacuum, clearly indicating that the only difference between the two forms is the extent of side group hydrogen bonding. Experimental results in the yellow form did not show the fluence-dependent slow component as observed in the red form of 4BCMU-PDA films.

Furthermore, the optical absorption spectra of the red film were measured before and after the intense laser pulse excitation. No difference was observed between two spectra, indicating that the structure change in the PDA thin films is reversible.

In conclusion, the slow relaxation component of 4BCMU-PDA red films in time-resolved DFWM measurements was found to be energy fluence dependent. Under intense light irradiation, the 4BCMU-PDA red films most likely experienced a transient reversible structural change originating from the side-chain intramolecular hydrogen bonding.

This work is supported by Air Force Office of Scientific Research grant No. 860031 and City College Faculty Award Program.

[1] G. M. Carter, M. K. Thakur, Y. J. Chen, and J. V. Hryniewicz, Appl. Phys. Lett. **47**, 457 (1985).

[2] G. M. Carter, J. V. Hrynuewicz, M. K. Thakur, Y. J. Chen, and S. E. Meyler, Appl. Phys. Lett. **49**, 998 (1986).

[3] B. I. Green, J. Orenstein, R. R. Millard, and L. R. Williams, in *Ultrafast Phenomena V*, edited by G. Fleming and A. Siegment (Springer, New York, 1986), pp. 472–474.

[4] D. Narayana Rao, Pratibha Chopra, Suniti K. Ghoshal, Jack Swiatkienwicz, and Paras N. Prasad, J. Chem. Phys. **84**, 7049 (1986).

[5] P. P. Ho, R. Dorsinville, N. L. Yang, G. Odian, G. Eichmamn, and R. R. Alfano, *Molecular and Polymeric Optoelectronic Materials*, edited by G. Khanarian, Proc. Soc. Photo-Opt. Instrum. Eng. **682**, 36 (1986).

[6] P. P. Ho, N. L. Yang, T. Jimbo, Q. Z. Wang, and R. R. Alfano, J. Opt. Soc. Am B **4**, 1025 (1987).

[7] T. Kanetake, Y. Tokura, and T. Koda, Solid State Commun. **56**, 803 (1985).

[8] E. Hanamura and N. Nagaosa, Solid State Commun. **62**, 5 (1987).

[9] Y. Tokura, K. Ishikawa, T. Kanetake, and T. Koda, Phys. Rev. B **36**, 2913 (1987).

[10] F. Bartoli, M. Kruer, L. Esterowitz, and R. Allen, J. Appl. Phys. **44**, 3713 (1973).

[11] Edward A. Collins, Jan Bares, and Fred W. Billmeyer, Jr., *Experiments in Polymer Science* (Wiley, New York, 1973).

[12] G. N. Patel, R. R. Chance, and J. D. Witt, J. Chem. Phys. **79**, 4387 (1979).