Observation of Reversible Photochemical "Blow Out" of the Third-Order Molecular Hyperpolarizability of Push−Pull Azo Dye in High Glass Transition Temperature Polyimides

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We present evidence of reversible optical control of the third-order molecular hyperpolarizability (γ) of nonlinear optical (NLO) azo chromophore. We show that optically-induced molecular shape change of the NLO dye from the trans to the cis form, by means of photoisomerization which occurs within the picosecond time scale, breaks γ down rapidly. The anharmonic movement of the electronic cloud of the NLO dye in strong optical field is "blown out" upon optical exitation of the azo chromophores. We show that γ recovers its initial value upon thermal back-isomerization of the dye to the trans form. This change in γ can be optically-cycled many times, leading to a novel all-optical light modulation phenomenon. The light polarization and molecular reorientation do not influence this all-optical switching of γ. We develop a theoretical model that considers a molecular density resulting from an intensity-dependent balance between two molecular species with different molecular third-order hyperpolarizabilities imbedded in a transparent medium. We derive analytical solutions, and we study the effect of the parameters involved in this all-optical process, including the irradiating light intensity and the change in magnitude and sign of γ. The theory explains the experimental findings and allows a physical insight into this optical control of third-order molecular hyperpolarizability of light sensitive nonlinear optical isomers.

1. Introduction

Organic materials are widely recognized as important candidates for the field of nonlinear optics.[1] Quadratic and cubic optical nonlinearities of polymer films containing molecules with appreciable molecular hyperpolarizabilities have been studied extensively for use in electro-optical and all-optical light modulation.[2−4] Incorporating photosensitive molecular units into polymers leads to photoreactive or macroscopically photoresponsive systems, the structural and/or optical (linear and quadratic) properties of which can be manipulated by light.[5,6] Photorefractivity in polymers has also been demonstrated,[7] and the photoisomerization of azobenzene derivatives has been shown to alter both the linear and quadratic NLO properties of azo polymers.[8−10] Here we show that the availability of high glass transition temperature (Tg) donor imbedded nonlinear optical (NLO) polyimide polymers allows the coupling between the photochemistry in NLO polymers and nonlinear optical effects to be extended to third-order effects. We report on the fast reversible optical command of the third-order molecular hyperpolarizability of push−pull diarylene azo dye, by means of photoisomerization which occurs within the picosecond time scale, incorporated through the donor substituent as a part of the polymer backbone in high Tg side chain NLO polyimides. In these polymers, the electron-donating group of the chromophore is incorporated directly into the backbone of the polymer without any flexible connector, which results in exceptional thermal and orientational stability.[11,12] We use electric field induced second-harmonic (EFISH) generation as an *in situ* probe to monitor the photochemical change in the third-order susceptibility of the polymer films.

In principle, the EFISH signal has contributions from both the second- and third-order nonlinearities, and the macroscopic EFISH third-order susceptibility $\chi^{(3)}_{\text{EFISH}}$ is related to the molecular quantities including the vectorial projection of quadratic hyperpolarizability along the dipole direction (β) and the component of cubic hyperpolarizability (γ) in an orientationally averaged model, according to the following relationship:

$$\chi^{(3)}_{\text{EFISH}} = \sum_{i=1}^{2} N_i \chi^{(3)}_{i,\text{EFISH}}, \quad \text{with} \quad \chi^{(3)}_{i,\text{EFISH}} = \langle \gamma_i^{\text{e}} + \gamma_i^{\text{v}} \rangle_{jj33} + \langle \beta \rangle_{jj3} \quad (1)$$

where $i = 1$ and 2 denote the polyimide matrix and NLO chromophore species, respectively, N_i values are number densities expressible as inverse specific volume, and the term ($\gamma_i^{\text{e}} + \gamma_i^{\text{v}}$) sums electronic, and hyper-Raman (or vibrational) contributions to EFISH. The subscript j denotes the laboratory axes (1, 2, 3), and the static field is directed along the 3-axis. Local field effects are included in the expressions of the hyperpolarizabilities. The term γ^{v} which is generally small has no contribution in EFISH, and the molecular vibrations are in the infrared.[13,14] The purely electronic nonlinearity γ^{e} has a frequency response out to the ultraviolet. The term $\langle \beta \rangle$ vanishes for centrosymmetric molecules or for systems where dipole rotation under dc field, or poling, is ineffective at the operating temperature. The latter appears to be the case for the particular polymers studied here, where both poling and photoassisted poling of the azo chromophores do not occur at room temperature:[15] In other words, the initial centrosymmetry of the polymer film is preserved at room temperature even when a dc field is applied to the polymer films, either with or without simultaneous irradiation. Therefore, third-order nonlinear optical effects can be independently studied in such polymers by means of EFISH. Under these conditions the EFISH signal

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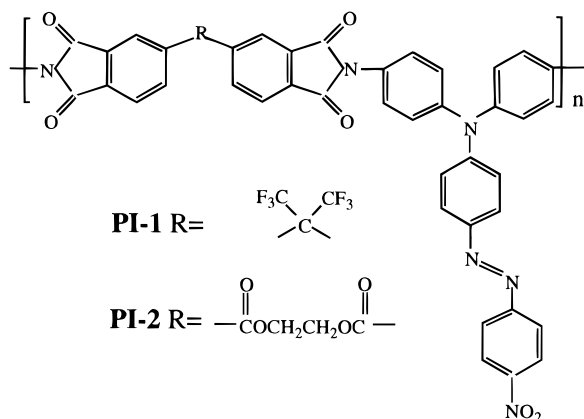
Figure 1. Chemical structures of the azo polyimide polymers.

results from the contributions of electronic nonlinearities dominated by the azo chromophore at second harmonic wavelength within the UV−vis spectral region, and the third-order nonlinearity is given by

$$\chi_{EFISH}^{(3)} = \sum_{i=1}^{2} N_i \langle \gamma_i^e \rangle_{jj33} \tag{2}$$

For anisometric molecules, which is the case of azo chromophores, of which the main component (γ) of the hyperpolarizability is along the long molecular axis, it is a good approximation to account for anisotropy that might exist in polymer films due to molecular alignment through the order parameters in eq 3.[8,16] Indeed, for uniaxial polymer films with a nonpolar order, the nonvanishing components of the $\chi^{(3)}$ tensor of each molecular species in terms of order parameters, namely A_2 and A_4, are

$$\chi_{3333}^{(3)} = N\gamma\left(\frac{1}{5} + \frac{4}{7}A_2 + \frac{8}{35}A_4\right) \quad \text{and}$$

$$\chi_{1133}^{(3)} = \chi_{2233}^{(3)} = N\gamma\left(\frac{1}{15} + \frac{1}{21}A_2 - \frac{4}{35}A_4\right) \tag{3}$$

For the sake of simplicity for the rest of the paper, the superscript e was dropped from the expression of the hyperpolarizability.

2. Experimental Section

The chemical structure of the polyimide polymers, henceforth referred to as PI-1 and PI-2 is given in Figure 1. Details of the polymer synthesis and characterization can be found in ref 12. The Tg values of the two polyimides shown in Figure 1 were determined by differential scanning calorimetry at a heating rate of 20 °C per minute. The Tg values for PI-1 and PI-2 were 350 °C and 252 °C, respectively.

Samples for the second-harmonic generation (SHG) experiments were prepared by spin-casting onto glass substrates. PI-1 was cast from a cyclohexanone solution and PI-2 from 1,1,2,2-tetrachloroethane. To remove the solvent after spin-casting, the PI-1 and PI-2 films were baked under vacuum for 1 h at 60 °C, followed by 1 h at 100 °C and 2 min at 220 °C in air. The thicknesses of the PI-1 and PI-2 films were, respectively, approximately 0.72 μm and 0.14 μm, and their respective optical densities were approximately 0.79 and 0.3 at 543.5 nm. A corona discharge was used to apply an electric field to the sample,[17] using approximately 5.5 kV applied to a thin tungsten wire held 1 cm above the polymer film. The substrate had an indium tin oxide coating on the opposite side which served as a ground. The conductivity of the glass is sufficiently large that the voltage drop is essentially entirely across the polymer

film, resulting in an applied field on the order of 2−3 MV/cm across a 1−2 μm thick polymer film.[17] Because corona does not require electrical contacts on the surface of the polymer, we used a SHG *in situ* probe to monitor the photochemical change in the third-order susceptibility of the PI-1 and PI-2 polymers.

Photoisomerization of the photochromic units was induced by irradiation with green light (wavelength 543.5 nm) from a helium−neon laser (Research Electro-Optics Inc.). This beam was linearly polarized in the vertical direction (polarization s), incident on the sample at approximately 24 degrees, with a 2 mm diameter spot. The polarization of this beam could be rotated from s to p and and back by using a half-wave plate, and the intensity for both polarizations was approximately 8 mW/cm². The fundamental for the second-harmonic (SH) probe was a Q-switched Nd:YLF laser (Quantronix Model 527) operating at 1053 nm with a 1 kHz repetition rate. The probe was linearly polarized, incident at 47 degrees near the Brewster angle which corresponds to the maximum SH signal, and focused to a spot smaller than and centered in the irradiation beam. A video camera was used to monitor the alignment of the beams and to ensure that the polymer film was not damaged during exposure. The polarization of the probe was controlled by using a half-wave plate and a polarizer leading to equal power for both s and p polarizations, and an analyzer was used for the SH light. The second-harmonic signal was isolated, detected by a photomultiplier, collected by a boxcar averager, and recorded by using a computer.

3. Results and Discussion

The effect of irradiation on the EFISH signal observed in PI-1 at room temperature is shown in Figure 2, where the top graphs and bottom graphs refer, respectively, to p- and s-polarized probes for both p (left)- and s (right)-irradiation. Similar results (not shown) were obtained for PI-2. This signal represents a pure $\chi^{(3)}$ or γ effect as mentioned previously. The term $\langle\beta\rangle$ does not contribute to the observed EFISH since application of a strong corona field to either polymer even at 150 °C does not result in any polar order.[15] This feature was anticipated by the high Tg value of the polymers. The photoinduced change of the molecular geometry of the NLO azo dye from the trans form to the cis form, which occurs within the picosecond time scale,[18] results in a drastic change of the third-order susceptibility of the PI-1 and PI-2 films as extensively discussed in the rest of the paper. We could not detect any photoconductivity in these films, and the same voltage was maintained on the sample during all the phases of the experiment.

Figure 2 also shows that when the irradiation light is turned off, the EFISH signal builds back up by means of the recovery of the cubic macroscopic susceptibility. The third-order molecular hyperpolarizability returns to the original γ_t (γ of the trans form) as a result of the recovery of the trans conformation of the azo chromophore caused by the cis ⟹ trans thermal back-reaction. The cis ⟹ trans thermally activated isomerization of the azo chromophores in both PI-1 and PI-2 exhibits a fast mean component on the order of seconds and a slower one ranging from minutes to hours.[19] Biexponential fits to the observed $\chi^{(3)}$ recovery during the cis ⟹ trans thermal back-isomerization for up to 500 s in several recovery cycles yielded mean values of 28 and 14 s, respectively, for the fast component in isomerized PI-1 and PI-2. The longer recovery time for PI-1 ranged from 289 to 390 s, while that for PI-2 varied from 66.8 to 167 s. The measured long recovery times are consistent with those found by the UV−vis studies of both PI-1 and PI-2 (6−12 min).[19]

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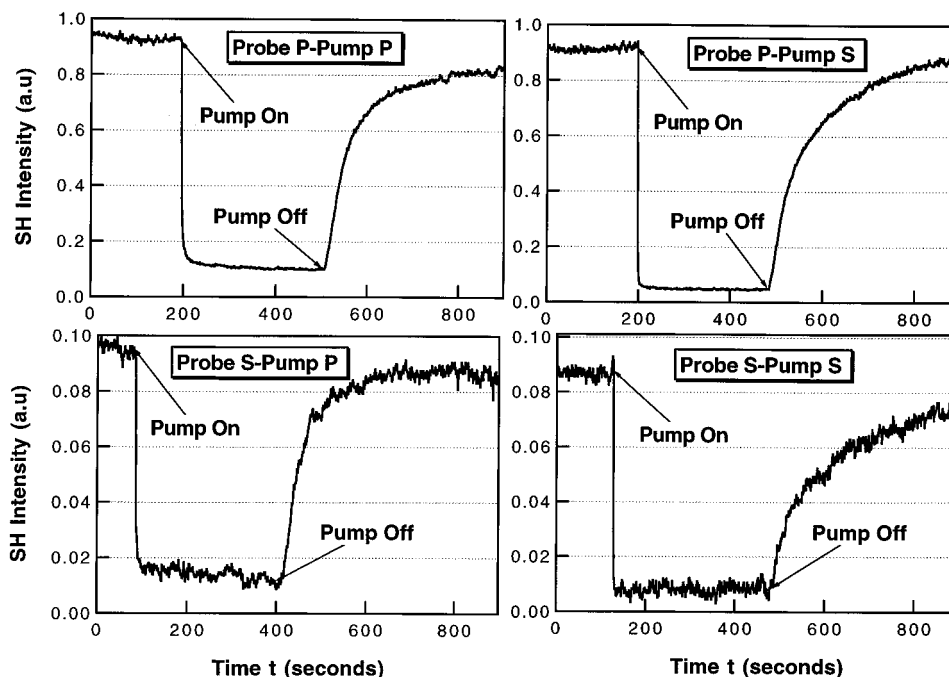*J. Phys. Chem. B, Vol. 101, No. 24, 1997* **4735**

Figure 2. Reversible rapid erase of the EFISH signal of the PI-1 polymer for four combinations of the irradiation and the probe polarizations, e.g. p (top)- or s (bottom)-probes and p (left)- or s (right)-irradiation.
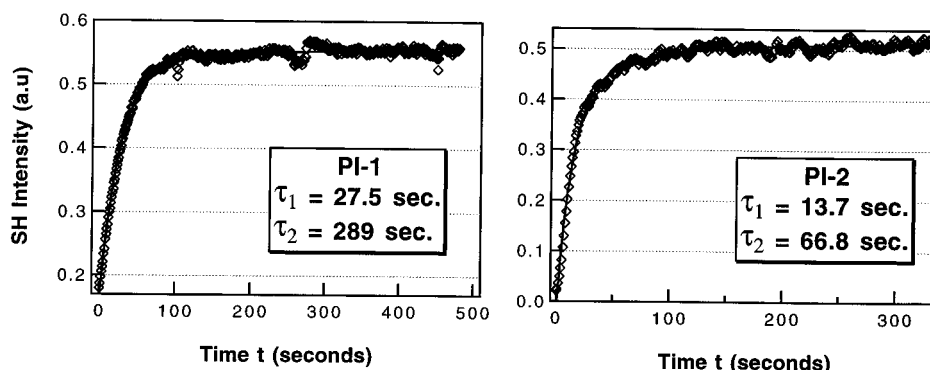

Figure 3. Example of biexponential fits (solid lines) to EFISH recovery (markers) during the cis $\Rightarrow$ trans thermal back-isomerization of the PI-1 (left) and PI-2 (right) polymers. The insets show the time constants of these biexponentials.

An example of this back-reaction is shown in Figure 3, where the solid lines show biexponential behaviors fitted to raw data of the recovery of the $\chi^{(3)}$ signal for both PI-1 (left) and PI-2 (right) over the first few hundred seconds. The time constants resulting from the fits are given in the insets. This reversible erase of γ can be repeated many times, resulting in all-optical modulation of the second-harmonic light (see Figure 4 for both PI-1 (top) and PI-2 (bottom)).

Next we discuss the dependence of the optically-induced decay of $\chi^{(3)}$ on the irradiating light intensity. Figure 5 shows the $\chi^{(3)}$ signal of PI-2 (top), and PI-1 (bottom) under various irradiation intensities (p-probe and s-irradiation for both the upper and the lower figure), where the numbers on the curves refer to the optical density used to attenuate the irradiation intensity. This shows that the $\chi^{(3)}$ strongly depends on the irradiation light intensity through an intensity-dependent photostationary state composed of a mixture of cis and trans isomers of the NLO chromophore. The chromophore exhibits an appreciable molecular hyperpolarizability γ at the SH wavelength only when the azo dye is in the trans form. The $\chi^{(3)}$ signal can be nearly completely extinguished by high irradiation intensity which results in a high cis isomer content. The SH wavelength falls within the visible absorption band of the photochromic chromophore, and the transparent polymer matrix
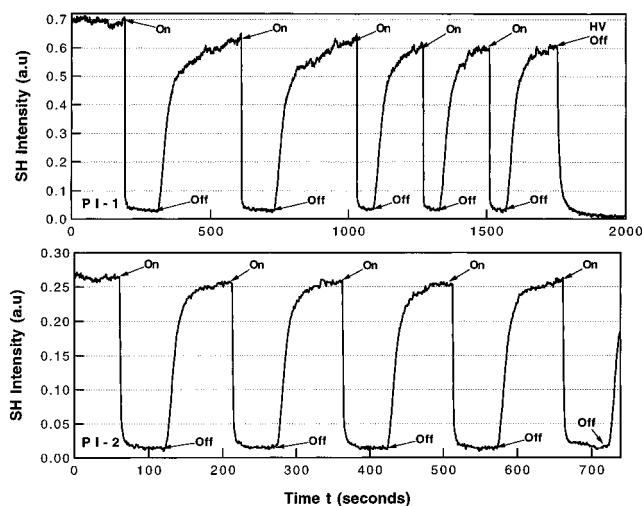

Figure 4. All-optical light modulation of the SH signal of the PI-1 (top) and PI-2 (bottom) polymers. The moments of turning the irradiating light on and off are indicated by arrows. HV Off in the top graph refers to the moment where the corona voltage was turned off.

does not contribute appreciably to the observed resonance-enhanced $\chi^{(3)}$ as has been shown for a series of azo dye containing polymethylmethacrylates.[20]
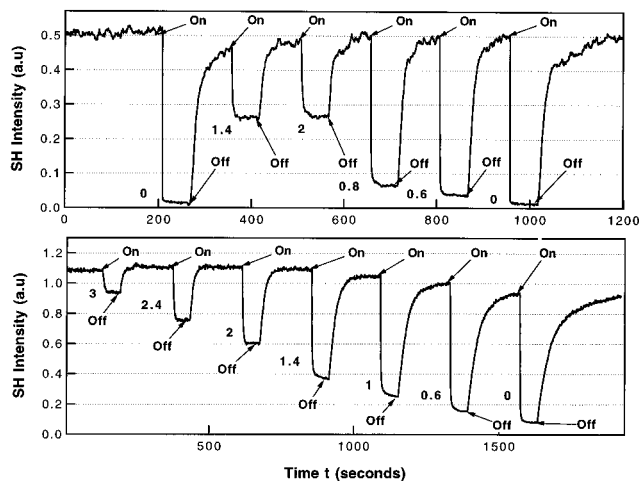
Figure 5. Effect of the irradiating light intensity on the EFISH signal of the PI-2 (top) and PI-1 (bottom) polymers. The moments of turning the irradiating light on and off are indicated by arrows, and the numbers on the figures refer to the optical density used to attenuate the intensity of the irradiating light.

Polarized light irradiation can reorient the azo chromophores in both PI-1 and PI-2.[19] This nonpolar orientation creates appreciable anisotropy in both polymers but does not noticeably influence this all-optical light modulation phenomenon. This is illustrated in Figure 2 for PI-1 for four combinations of the irradiation and the probe polarizations, e.g. p (top)- or s (bottom)-probe and p (left)- or s (right)-irradiation. Similar results were obtained for PI-2 (not shown). One can see that both s- and p-irradiation produce the same effect on the $\chi^{(3)}$ decay for both s- and p-polarizations of the probe beam. This noninfluence of polarized irradiation is not by means of saturation effects since attenuated irradiation produces similar results (not shown). We checked that the SH light is always p-polarized regardless of the input polarization of the fundamental beam,[17] and we found that neither s- nor p-irradiation of the PI-1 and PI-2 films induces a phase shift of the SH light at any stage of the irradiation; in other words s-polarized SH was not detected. Furthermore one can see from Figure 2 that the relative ratio of p- and s-SH intensities is about 9, which gives a value of 3 for the relative ratio of s- and p-cubic susceptibilities (see eq 3) prior to or at eventual irradiation (note that $I_{SH} \propto |\chi^{(3)}|^2$). If anisotropy exists, its contribution to the effects observed here is negligible. Therefore in eq 3 one can neglect the order parameters A_2 and A_4 which characterize anisotropy. We conclude that the third-order molecular hyperpolarizability of the azo chromophore breaks down by means of photochemical change of the chromophore molecular shape from the trans form to the cis form as further discussed next.

The very fast decrease shown in Figures 2−5 at the moment where the sample is irradiated is due to the rapid rearrangement of the electronic cloud during the trans ⟹ cis photochemical conversion of the photochromic dye (see Figure 6). Trans ⟹ cis photoisomerization of azobenzenes have been shown to occur within the picosecond time scale,[18] and there is evidence that EFISH decay can be induced with nanosecond pulses.[10] Photochemical molecular shape change of the NLO dye breaks down rapidly, or "blows out", the strong optical field driven anharmonic movement of the electronic cloud of the NLO dye, which can be reversed upon back-isomerization of the dye to the trans form. This decrease clearly shows that the magnitude of γ_c (γ of the cis form) is negligible in comparison to that of γ_t at the SH wavelength. Indeed, in an extreme hypothetical case where γ_c and γ_t are of comparably appreciable magnitudes and opposite signs at the SH wavelength, the $\chi^{(3)}$ signal would
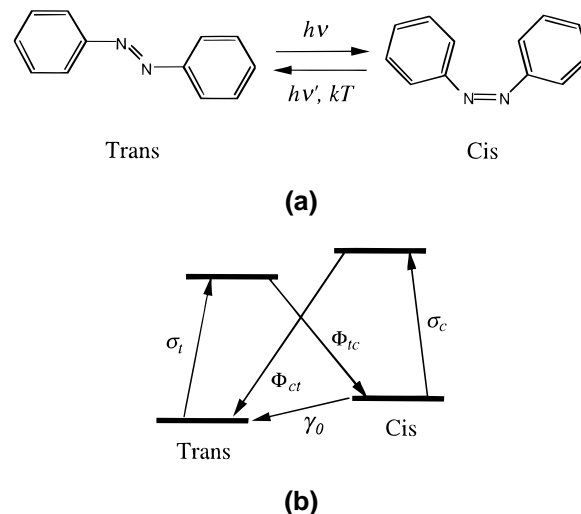

Figure 6. (a) Trans ⟷ cis isomerization of azobenzenes. (b) Simplified model of the molecular states. Only two excited states have been represented, but each of them may represent a set of actual levels: we only assume that the lifetime of all these levels is very short. σ_t and σ_c are the cross sections for absorption of one photon by a molecule in the trans or the cis state, respectively. γ_0 is the thermal relaxation rate. ϕ_{ct} and ϕ_{tc} are the quantum yields of photoisomerization; they represent the probability per absorbed photon of the photochemical conversion.

resume under irradiation only if the ratio of trans (N_t) and cis (N_c) populations at the photostationary state, e.g. N_t/N_c, matches exactly the ratio of cis and trans molecular hyperpolarizabilities, e.g. $-\gamma_c/\gamma_t$ (see relation 5 also). This ratio only depends at a given wavelength on the molecular shape, and leads to the nonrealistic possibility where N_t/N_c would not depend on the irradiation intensity (see model below also). Furthermore, these extreme conditions would imply a SH signal that decreases at the early stage of the irradiation and eventually recovers at high cis isomer content for long irradiation times as mathematically shown next. This further contradicts the experiments which show that SH intensity decreases with the intensity of irradiation and almost vanishes at high intensity of irradiation (see Figure 5). This lends support to γ_t as the only appreciable molecular hyperpolarizability at the SH wavelength, and is anticipated by the conformation of the cis isomer of the NLO dye which is more globular and less conjugated than the trans form (see Figure 6). Theoretical calculations have shown that the ground state dipole moment and the second-order molecular hyperpolarizability of disperse red 1 (DR1), a dye similar to the chromophore studied here, which are appreciable for the trans form are significantly small for the cis form.[21] The fact that γ_c is smaller than γ_t is further confirmed by the next theoretical discussion.

4. Theoretical Model for Steady State and Transient Properties

Next we introduce a simple model that considers a total molecular density N resulting from an intensity-dependent balance between two molecular species with different molecular hyperpolarizabilities imbedded in a transparent medium, e.g. trans (N_t, γ_t) and cis (N_c, γ_c), respectively.

Azobenzene derivatives may exist as two geometric isomers, the trans and the cis forms (Figure 6a). The photoisomerization reaction begins by elevating molecules to electronically excited states, followed by nonradiative decay back to the ground state in either the cis or trans forms. The ratio of cis/trans states is dependent on the quantum yield of the appropriate photoisomerization reaction (e.g. ϕ_{tc} and ϕ_{ct} for the direct trans ⟹ cis and reverse cis ⟹ trans photoisomerization reactions, respectively

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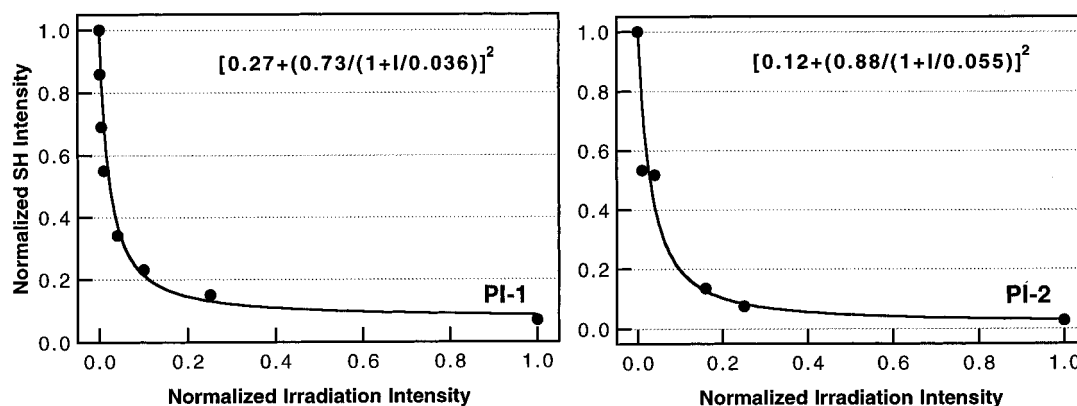*J. Phys. Chem. B, Vol. 101, No. 24, 1997* **4737**

Figure 7. Hyperbolic fits to the SH intensity at the photostationary state of irradiation *versus* the irradiating light intensity for the PI-1 (left) and PI-2 (right) polymers. The insets show the functions corresponding to the fits. See the text for more details.

(see Figure 6b)). As the trans isomer is generally more stable than the cis isomer (for azobenzenes the energy barrier at room temperature is about 50 kJmol^{-1}), molecules in the cis form may convert to the trans form by one of two mechanisms: (1) a spontaneous thermal back reaction or (2) a reverse cis $\Rightarrow$ trans photoisomerization cycle.

The governing equation for trans and cis populations resulting from the four-level model of Figure 6b is

$$dN_t/dt = -\sigma_t\phi_{tc}IN_t + (\sigma_c\phi_{ct}I + \gamma_0)N_c, \quad \text{with} \quad N_t + N_c = N \tag{4}$$

where I is the irradiating light intensity expressed in number of photons per second per cm^2 and σ_t, σ_c, ϕ_{ct}, ϕ_{tc}, and γ_0 are defined in the caption to Figure 6. Assuming that the polyimide matrix does not appreciably contribute to the resonance-enhanced EFISH and neglecting orientational effects, the population evolution for the molecular system, if the irradiating light is turned on at the time $t = 0$ is

$$\frac{N_t(t)}{N} = \frac{a}{b}\exp(-bt/\tau_c) + c \tag{5}$$

and the cubic susceptibility is

$$\frac{5\chi_{3333}^{(3)}(t)}{N\gamma_t} = A\exp(-bt/\tau_c) + B$$

with $A = (1 - \rho)a/b$, $B = \rho(1 - c) + c$, and $\chi_{3333}^{(3)} =$

$$3\chi_{1133}^{(3)} = 3\chi_{2233}^{(3)} \tag{6}$$

where $\rho = \gamma_c/\gamma_t$, $a = \sigma_t\phi_{tc}\,\tau_c/\tau_p$, $b = 1 + a(1 + \alpha)$ and $c = (1 + a\alpha)/b$, τ_c is the cis lifetime which is imposed by the rate of the cis $\Rightarrow$ trans thermal back-reaction, τ_p is the pumping time (equal to the inverse of the irradiating-light intensity I), and $\alpha = \sigma_c\phi_{ct}/\sigma_t\phi_{tc}$ represents the competition between the back and forth photoisomerization reactions. The initial conditions are, at the time $t = 0$, $N_t(t{=}0) = N$, $N_c(t{=}0) = 0$, and $5\chi_{3333}^{(3)}(t = 0) = N\gamma_t$ and, at the steady state, $N_t(t{=}\infty) = cN$, $N_c(t{=}\infty) = (1-c)N$, and $5\chi_{3333}^{(3)}(t = \infty)/N\gamma_t = B$.

Equation 6 was obtained by substituting the expressions of N_c and N_t from eqs 4 and 5 in the total third-order susceptibility $\chi^{(3)}$ which is given by

$$5\chi_{3333}^{(3)} = N_t\gamma_t + N_c\gamma_c \tag{7}$$

From the above relation it is concluded that the macroscopic susceptibility should follow a hyperbolic law as a function of the irradiating light intensity I, by assuming that ρ does not

depend on I and by noting that $c = (\alpha + (1 + I/I_s)^{-1})/(1 + \alpha)$, where $I_s = (\sigma_c\phi_{ct} + \sigma_t\phi_{tc})\alpha\tau_c$ denotes the saturation intensity. Indeed, Figure 7 shows hyperbolic functions that were adjusted to the experimental data, giving the variation of the SH intensity (I_{SH}) at the steady state of the irradiation *versus* the irradiation intensity for both PI-1 (left) and PI-2 (right). This shows that theory agrees with experiment and confirms that ρ does not depend on the irradiation intensity.

The recovery of $\chi^{(3)}$ during the cis $\Rightarrow$ trans back-isomerization is, if the irradiation is turned off at the time (different from that describing the dynamics of irradiation) $t = 0$,

$$\frac{5\chi_{3333}^{(3)}(t)}{N\gamma_t} = 1 + (\rho - 1)(1 - c)\exp(-t/\tau_c) \tag{8}$$

The initial conditions for the recovery of $\chi^{(3)}$ read: $5\chi_{3333}^{(3)}(t = 0)/N\gamma_t = B$ and $5\chi_{3333}^{(3)}(t = \infty)/N\gamma_t = 1$. These theoretical expressions reproduce the behaviors reported in Figures 2–5, which unambigiuously confirms that $\chi^{(3)}$ recovers its magnitude prior to irradiation by means of the recovery of the third-order molecular hyperpolarizability of the trans form upon back-isomerization.

Figures 8–10 are computer simulations of all-optical light modulation based on the analytical solutions of the model discussed above. In these figures, $\chi_{3333}^{(3)}$ is normalized by $N\gamma_t$, and the time t and τ_p are normalized by the cis lifetime. The times where the light is switched on and off are indicated by arrows. The insets in the figures show the τ_p, α, and ρ that were used. Figure 8 (left) reproduces the experiments reported in Figure 4. Figure 8 (right) shows an expanded view of the decay of the third-order nonlinearity at the early stage of the irradiation. For Figures 8 and 9, we assumed parameters consistent with the DR1 molecules,[21] e.g. the cis absorption cross section two times smaller than that of the trans isomer at the irradiating wavelength, $\phi_{tc} = 0.7$, and $\phi_{ct} = 0.11$. The simulation of Figure 8 was performed with a value as small as $\rho = 0.1$. This theory clearly confirms the above discussions regarding the reversible photochemical rapid erase of the third-order molecular hyperpolarizability of the azo chromophore and reproduces the experimental observations.

Figure 9 shows the influence of the (a) increase of magnitude and (b) inversion of sign of ρ on the transients of $\chi^{(3)}$ and I_{SH} upon a cycle of irradiation and recovery. These behaviors are obviously not observed for the azo dye studied in this paper; they contradict the experiments and confirm the discussions of the previous section regarding the effect of change of ρ on the dynamics of the light modulation of γ. However, other photochromic molecules may show such dynamics. The effect
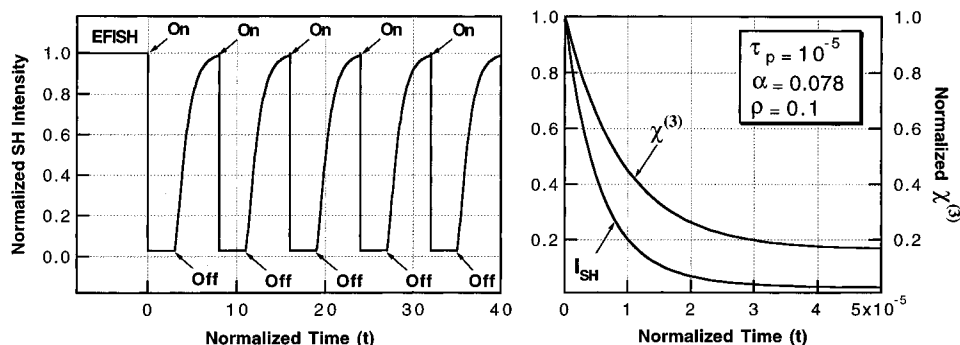
Figure 8. (left) Computer simulation of all-optical light modulation following the azo chromophore third-order nonlinearity "blow out"/recovery cycling model. (right) Expanded view of the early stage of the irradiation. The parameters used for the calculations are given in the inset. See the text for more details.
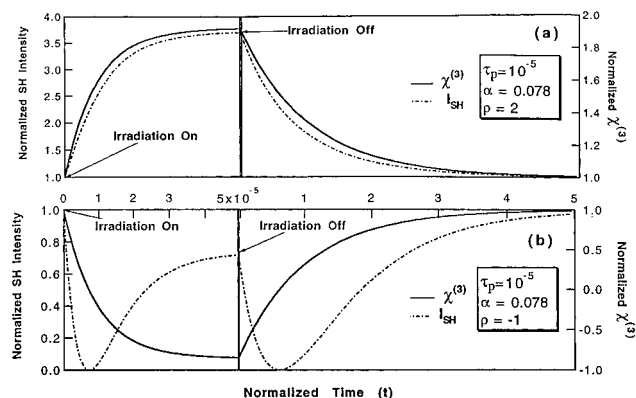

Figure 9. Computer simulation of EFISH switching for a hypothetical optically-induced increase of γ (a) and a change of sign of γ (b). Full and broken lines refer to $\chi^{(3)}$ and I_{SH}, respectively. The parameters used for the calculations are given in the inset. See the text for more details.
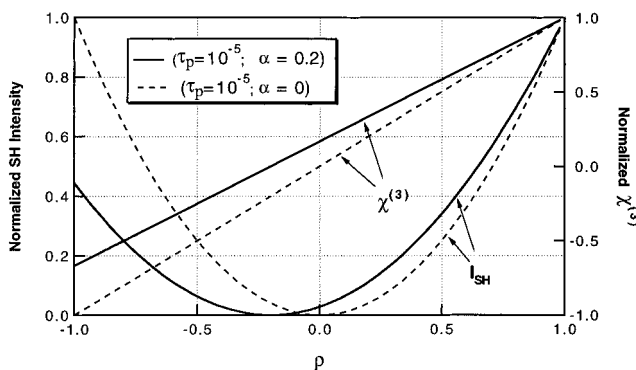

Figure 10. Computer simulation of the effect of hypothetical optically-induced change of γ on the EFISH signal at the steady state of the irradiation. $\chi^{(3)}$ and I_{SH} are shown by arrows, and full and broken lines correspond to different values of α. The parameters used for the calculations are given in the inset. See the text for more details.

of the change of ρ on the steady state properties of the γ switching process is reported in Figure 10 for two values of α. A change in α slightly shifts the steady state value of the $\chi^{(3)}$ (or I_{SH}) signal (see also Figures 8 and 9). Most important is to note that no modulation of $\chi^{(3)}$ (or I_{SH}) is possible if there is no change, in sign or magnitude, of γ of the photochromic dye at hand upon irradiation. This can be seen from Figure 10 at the values of $\chi^{(3)}$ and I_{SH} for ρ equal to 1.

5. Conclusion

In summary this work reports about reversble optical control of the third-order molecular hyperpolarizability of a molecule that can be reversibly isomerized. The process is the reversible breakdown of the anharmonic movement of the electronic cloud of the push−pull NLO chromophore, in strong optical field, which correlates to the photochemical control of the chromophore shape, as shown experimentally and confirmed theoretically. We have shown that EFISH experiments can be extended to study pure third-order effects even for noncentrosymmetric chromophores presenting appreciable ground state dipole moment and second-order hyperpolarizability. While such chromophores have to be introduced in specifically engineered high Tg polymers, centrosymmetric photochromic dyes could, in principle, be used even in solutions. We introduced a theoretical model which explains the experimental findings and allows a physical insight into the optical command of third-order molecular hyperpolarizability of light sensitive nonlinear optical chromophores. We derived analytical solutions, and we investigated the effects of the parameters involved in this all-optical process, including the irradiating light intensity and the change in magnitude and sign of γ. This theory is general and can be used for other photochromic systems showing optically-induced γ−switching. Depending on application, this reversible light-induced cycling of the cubic susceptibility of such photochromic polyimide materials might have utility, e.g. imaging reversible patterns of $\chi^{(3)}$ areas may be of particular interest for all-optical light modulation. The fact that the ground state dipole moment and molecular hyperpolarizability can be controlled by the photoisomerization process which occurs within the picosecond time scale might lead to polymer systems operating in this time range and may improve the response time of polymers for optical data storage which utilizes photoinduced orientation or the photorefractive effect.

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