Ultrafast time response of optical nonlinearity in polysilane polymers

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Ultrafast relaxation kinetics of third-order nonlinear susceptibility $\chi^{(3)}$ of polysilane polymers was measured using both the picosecond Kerr gate and forward degenerated four-wave mixing. The relative contributions from various nonlinear decay mechanisms were estimated from the time response. The third-order nonlinear response was measured to be faster than 3 ps arising from electronic mechanism. A slower component is assigned to the refractive index grating due to light pressure.

Organic polymers with large and fast nonlinearities are becoming potential candidates for applications in optical computational and imaging devices. The most promising candidates are one-dimensional conjugated π electron systems, such as polydiacetylenes. Recently, attention has been paid to polysilanes whose backbone consists entirely of silicon atoms. The third-order nonlinear susceptibility $\chi^{(3)}$ of polysilane was measured to be comparable to that of polydiacetylenes in the nonresonance regime. Polysilane is transparent in the visible region where polydiacetylenes are highly absorbing. These, together with the facility of producing good quality thin films, make polysilane a new interesting nonlinear material.[1,2] In the past, $\chi^{(3)}$ of polysilane thin films was obtained primarily by third-harmonic generation measurements and four-wave mixing with nanosecond laser pulses without any time resolution. In this letter, we report on the temporal behavior of $\chi^{(3)}$ of polysilane in thin films and solutions using both the picosecond time resolution Kerr gate and four-wave mixing. The relative contributions from various nonlinear mechanisms were separated by the kinetic measurements.

The polysilane polymer with molecular structure $[\phi\text{-Si-}(CH_3)]_n$ was synthesized by the method described in Ref. 3. The film casting of polyphenylmethylsilane was prepared on a large crystallization dish with controlled vapor pressure of organic solvents [toluene, tetrahydrofuran (THF)]. In these polymers, each monomer unit is composed of a central Si bonded to a methyl group (CH_3) and a large "side group" ϕ. All monomers are σ bonded to each other through the silicon atoms to form the polymer chain. This type of bonding results in Si—Si σ-electron delocalization.[4] A typical optical absorption spectrum of polysilane is displayed in Fig. 1. The spectrum shows that there is no apparent absorption from 360 to 1060 nm.

Picosecond optical Kerr gate (OKG) was used to determine the nonlinear optical kinetics of polysilane thin films and solutions. The single optical pulses with ~8 ps (full width at half-maximum) duration were generated from a mode-locked Nd:glass laser with a single-pulse selector, an amplifier, and a second-harmonic generator. The pump and probe wavelengths were at 1060 and 530 nm, respectively. The detail geometry of OKG is described in Ref. 5. The time resolution for this OKG was determined to be about 3 ps from the rise and decay time slopes of the Kerr signal profile of CS_2.

The normalized transmitted signal $I(\tau_D)$ through a (10 ± 1.0) μm polysilane thin-film Kerr gate as a function of the time delay τ_D between the pump and probe pulses is displayed in Fig. 2. The slopes of the rise and decay of Kerr signal profile are 3 ps. Therefore, the relaxation time of $\chi^{(3)}$ process of polysilane thin films was unresolved (<3 ps). The Kerr signal profile for solutions is identical to Fig. 2.

The transmitted Kerr signal through a Kerr medium as a function of delay time τ_D between the probe and pump pulses is given by

$$I(\tau_D) = \int_{-\infty}^{\infty} \langle E^2_{\text{probe}}(t-\tau_D)\rangle \sin^2 \frac{\delta\phi_{(t)}}{2}\, dt. \qquad (1)$$

In general, the total induced phase retardation[5] at the peak value ($\tau_D = 0$) is obtained through the integration over the sample length L:

$$\delta\phi_{(0)} = \frac{2\pi}{\lambda_2}\frac{n_2 I_1}{\alpha_1}(1 - e^{-\alpha_1 L}), \qquad (2)$$

for a Kerr medium with the relaxation time faster than the laser pulses duration and with absorption coefficients α_1, α_2 at pump and probe wavelengths, respectively.

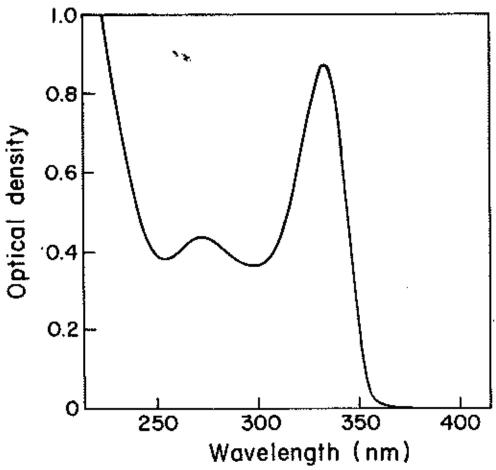

FIG. 1. Optical absorption spectrum of polysilane solution with concentration of 6.7×10^{-5} g/ml.

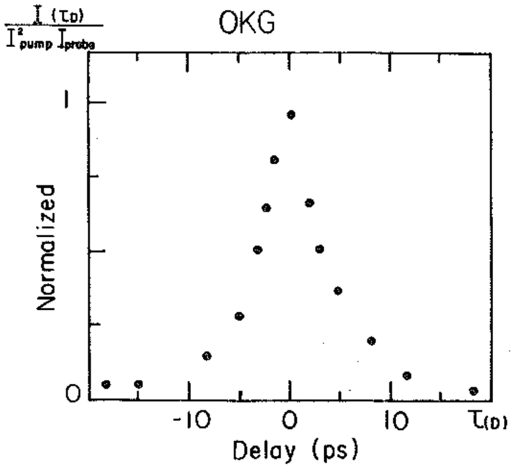

FIG. 2. Normalized time-resolved Kerr transmitted signal from polysilane thin films using 8 ps laser pulses. Both rise and decay slopes are 3 ps. The pump and probe wavelengths are at 1060 and 530 nm, respectively.

When $\delta\phi \ll 1$, the peak value of transmitted Kerr signal is approximately given by

$$I_{(0)} \sim \left(\frac{2\pi}{\lambda_2 \alpha_1}\right)^2 n_2^2 [1 - e^{-\alpha_1 L}]^2 e^{-\alpha_2 L} I_1^2 I_2, \quad (3)$$

where λ_2 is the probe wavelength.

Equation (3) can be simplified to

$$I_{(0)} \sim (2\pi/\lambda_2)^2 n_2^2 L^2 I_1^2 I_2, \quad (4)$$

since the sample absorption at pump and probe wavelengths is negligible.

The nonlinear index of refraction n_2 is related to $\chi^{(3)}$ by

$$n_2 = (2\pi/n_0)\chi^{(3)}_{1212}. \quad (5)$$

The value of the third-order nonlinear susceptibility $\chi^{(3)}$ was measured to be on the order of $2.0 \pm 0.6 \times 10^{-12}$ esu from the peak value of the OKG.

The relaxation kinetics of $\chi^{(3)}$ of polysilane solutions was also determined by the forward degenerated four-wave mixing (DFWM) technique in the phase-matched three-dimensional configuration (see the inset of Fig. 3). In this case, the excitation source was a 10 Hz mode-locked Quantel YAG laser pulses with 30 ps duration at 530 nm. The temporal evolution of the generated fourth beam $\mathbf{K}_4$ was measured by varying the arrival time (delay time) of one incident beam $\mathbf{K}_2$ (probe beam) relative to the other two beams $\mathbf{K}_1, \mathbf{K}_3$ (pump beams) via a stepper-driven optical delay line. In these measurements, all three beams are polarized parallel to the y axis. The signal from the solvent (THF) was below the detection threshold.

The intensity I of the fourth beam $\mathbf{K}_4$ (signal) as a function of the delay time was measured and displayed in Fig. 3. The signal profile consists of a fast and a weak slow component. The fast component is clearly unresolved (<20 ps) in agreement with the OKG data. It took certain time (on the order of >0.1 s, several successive pulses) to build up the grating responsible for the weak slow component in the solution. Once the grating was formed, the signal was independent of the delay time up to 1 ns which is the maximum delay time of our delay line. The origin of weak slow component will be discussed after estimating $\chi^{(3)}$.

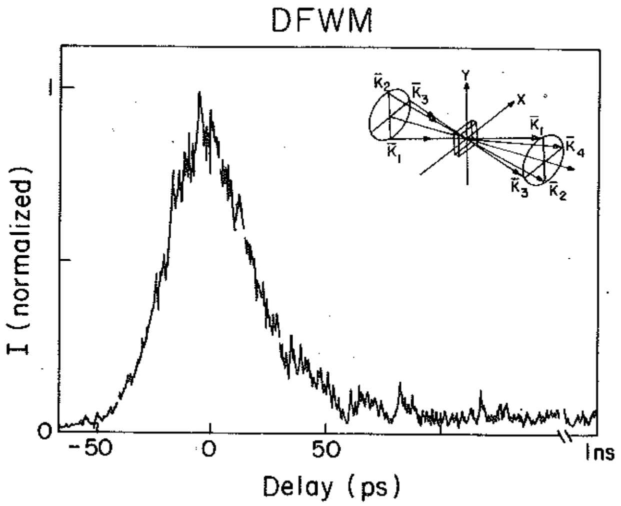

FIG. 3. Normalized intensity of DFWM signal from polysilane solution as a function of the delay time between probe and pump pulses. The excitation wavelength is at 530 nm. The inset indicates the wave vector diagram of DFWM configuration.

By integrating the equation for the power in the fourth beam generated per unit length in the sample and neglecting absorption at 530 nm, $\chi^{(3)}$ is given by[6]

$$\chi^{(3)}_{1111} \sim \frac{cn^2}{32\pi^2}\left(\frac{\lambda_0 \omega_0{}^2}{2\tau L}\right)\left[\left(\frac{45}{8}\right)\frac{E_4}{E_1 E_2 E_3}\right]^{1/2}, \quad (6)$$

where E_i is the pulse energy of the ith beam, ω_0 is the laser beam waist at the focus, and τ is the pulse width. The calculated $\chi^{(3)}$ of the fast component is estimated to be on the order of $1.6 \pm 0.2 \times 10^{-12}$ esu. This value is in good agreement with the value obtained from OKG experiment.

The observed large value of cubic susceptibility of polysilane most likely arises from the electrons delocalized in the polymer backbone and from the transition dipole moments parallel to the molecular axes. The fast decay (<3 ps) which is unresolved by our measurements points to an electronic contribution.[1,2]

The slow component could arise from a thermal grating formed by two-photon absorption in the solution or the spatial motion of polysilane molecules caused by diffusion in the optical field gradient. The decay of the thermal grating is related to the thermal parameters of the solvent THF by[7]

$$\tau = \rho C_p \Lambda^2 / 4\pi^2 K, \quad (7)$$

where ρ is the density, C_p is the heat capacity, K is the thermal conductivity, and Λ is the grating space. The grating space is obtained from $\Lambda = \lambda / 2n \sin(\theta/2)$, where θ is the angle between the pump beams. Substituting these parameters into Eq. (7), τ is obtained on the order of 10^{-5} s which is much faster than the experimental observations. This is reasonable since the probability of two-photon absorption in the solution is small.

An alternative model to explain the slow component arises from the radiation pressure. The polysilane molecules in the optical field E acquire an induced polarization $P = \alpha E$. The radiation pressure from the laser light produces a force[8] $\sim \alpha \nabla \mathbf{E}^2$ acting on the polysilane molecules which causes the molecules to move into the high-light intensity regions since $n_{\mathrm{polysilane}} > n_{\mathrm{THF}}$. The increasing density of the molecules in the high-field regions increases the average refractive index, thus creating a refractive index grating in the material. The thermal Brownian diffusion of the molecules opposed the motion from light force, which will tend to wash out the optically formed grating. The grating decay time which is approximately the time for the molecules to diffuse one quarter of the grating space Λ is given by[8]

$$\tau = 3\pi r\eta\Lambda^2/16kT, \tag{8}$$

where η is the viscosity of the solvent THF(0.438 cP), k is the Boltzmann constant, T is the absolute temperature, and r is the radius of polysilane molecules. The polysilane molecule has been shown to have an unusually high characteristic ratio C_∞,[9] and is considered here as an extended coil, having a hydrodynamic radius of ~ 600 Å. The calculation from Eq. (8) gives $\tau = 0.4$ s. The formation time for the grating is roughly on the same order of magnitude as the observed decay time under our experimental condition.[8] The absence of slower components of polysilane solution in OKG measurement is consistent with the radiation pressure model since OKG measurement was performed with single laser shot at greater than 2 min rate.

In conclusion, the electronic part of $\chi^{(3)}$ of polysilane is measured to be $\sim 1.6\times 10^{-12}$ esu in good agreement with previous observations.[1,2] The response time of nonlinear optical process associated with electronic mechanism is found to be faster than 3 ps. The slower component in polysilane solution is assigned to the refractive index grating arising from the radiation pressure.

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