Femtosecond dynamics of the nonlinear optical response in polydiethynylsilane

K. S. Wong, S. G. Han, and Z. V. Vardeny
Department of Physics, University of Utah, Salt Lake City, Utah 84112

J. Shinar, Y. Pang, S. Ijadi-Maghsoodi, and T. J. Barton
Ames Laboratory-USDOE, Physics and Chemistry Departments, Iowa State University, Ames, Iowa 50011

S. Grigoras and B. Parbhoo
Dow Corning Corporation, Midland, Michigan 48686

We have measured the femtosecond dynamics of the nonlinear optical response $\chi^{(3)}$ in polydiethynylsilane $(C_4H_2SiBu_2)_x$, a novel class of π-conjugated polymers incorporating Si, using degenerate four-wave mixing and photoinduced absorption techniques. In resonance conditions at 620 nm we found $\chi^{(3)} = 3 \times 10^{-9}$ esu, which decays in a record time of 135 fs, followed by a slower decay component of 750 fs, without a long tail even at high laser intensities. This material is an excellent candidate for nonlinear optical devices in the sub-THz frequency range.

Materials with large and fast optical response are needed for the future of optical communication, imaging and computation devices.[1] π-conjugated polymers have recently been the focus of wide interest as nonlinear optical materials[2] with potential applications as fast optical switches and modulators.[3] This is mainly due to the strong enhancement of the nonlinear optical susceptibility $\chi^{(3)}$ caused by the polymer quasi-one-dimensional (1-D) backbone structure, the relatively fast optical response, and the ease of processibility. However, these properties do not necessarily exist simultaneously in each π-conjugated polymer. Polyacetylene, for example, is not soluble nor stable in air.[4] Polydiacetylene[5] and polythiophene[6] have long tails in their transient optical responses at high laser illumination and the response of polyaniline is quite slow with long tailing even at low laser intensities.[7]

In this letter we introduce a new π-conjugated polymer, polydiethynylsilane (PDES): $(C_4H_2SiBu_2)_x$, which has all the desired properties for its use in applications of nonlinear optics. PDES is soluble and therefore easy to process; it is also stable in air. We find that PDES has a large $\chi^{(3)}$ (3×10^{-9} esu) in resonance conditions (at 620 nm); its transient optical response (135 fs) is one of the fastest ever measured in conducting polymers in resonance conditions. It is followed by a very short tail of order 2 ps. This polymer therefore seems to be an excellent candidate for optical modulators and switches in the subterahertz frequency range.

$R_2 Si$ ($C\equiv CH)_2$ monomers, where R = phenyl (Ph), methyl (Me), butyl (Bu), or hexyl (Hex), were polymerized by $MoCl_5$ catalysis.[8] Weight average molecular weights ranged from $\sim 100\,000$ (~ 450 monomers/chain) in the diphenyl to values in excess of 2×10^5 (~ 1500 monomers/chain) in the Bu-PDES. The polymers are soluble in various organic solvents, easily cast into films and are apparently quite stable in air. Detailed ^{13}C and ^{29}Si nuclear magnetic resonance and resonant Raman scattering measurements,[9] together with *ab initio* Hartree–Fock calculations of the backbone structure, indicate a four-

membered backbone ring structure, as depicted in the inset of Fig. 1. The two dimerizations shown were calculated[10] to be degenerate to within ~ 4 meV. Since alternate C atoms of the backbone are bonded to Si, the on-site lattice potential of the π orbitals is expected to alternate in a manner similar to the hypothetical degenerate ground state diatomic $(AB)_x$ polymer envisaged by Rice and Mele.[11] As such, PDES should support solitons[11] and polarons[12] as primary electronic excitations, followed by major shifts in the optical oscillator strength; the latter effect has been recently suggested[13] to enhance the value of $\chi^{(3)}$ in π-conjugated polymers.

The optical absorption of a Bu-PDES film is shown in Fig. 1. It has a shoulder at 2 eV followed by a maximum at 2.2 eV, believed to be a phonon sideband; we thus place the energy gap at 2 eV. A relatively sharp absorption tail and absence of significant absorption bands below 1.5 eV clearly indicate a quasi-1-D electronic system and low density of defects within the gap.

The experimental setup for measuring $\chi^{(3)}$ (ω; ω, $-\omega$, ω) consisted of a CPM dye laser whose short pulses were amplified by 10^5 by a dye/copper vapor laser optical amplifier with a repetition rate of 8 kHz. After passing through two pairs of prisms to compensate for the dispersion in the dye amplifier, the pulse duration was reduced to 90 fs at 620 nm (2 eV) with pulse energy of 5 μJ; attenuators were used to reduce the power level at the sample to less than 10 GW/cm^2 to avoid sample damage. $\chi^{(3)}$ (ω) was measured by the transient degenerate four-wave mixing (DFWM) technique in the folded box CARS configuration.[6] This was done by splitting the laser beam into three: two parallel polarized writing beams (I_1 and I_2) which were temporally and spatially overlapped onto a 50 μ spot on the sample forming the transient grating, and a reading beam (I_3) which was modulated by a chopper at 1 kHz and time delayed by a translational stage with 0.5 fs resolution. The diffracted beam intensity (I_4) was measured as a function of the delay τ in I_3 by a Si detector and lock-in amplifier. The magnitude of $\chi^{(3)}$ was calculated by
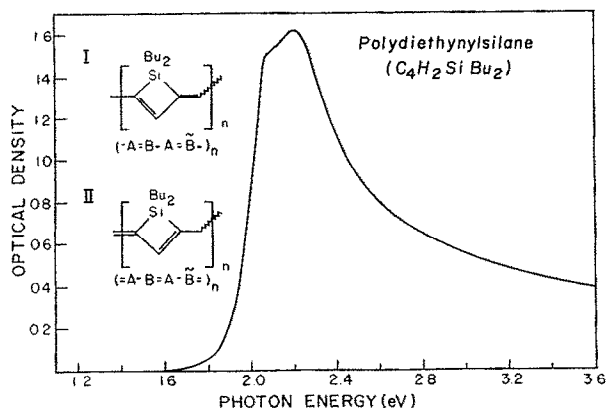
FIG. 1. Optical absorption spectrum of Si(Bu)$_2$- PDES. The two nearly degenerate dimerizations are shown schematically.

comparing I_4 to a reference signal $I_{4,r}$ of a CS$_2$ liquid measured under identical experimental conditions, using the equation:[6,14]

$$\chi^{(3)} = \chi_r^{(3)} \gamma (I_4/I_{4,r})^{1/2}, \qquad (1)$$

where $\chi_r^{(3)}$ ($= 8.8 \times 10^{-13}$ esu) refers to CS$_2$ and $\gamma = \alpha n^2 L_r/n_r^2 \sqrt{T}(1-T)$, $T = \exp(-\alpha L)$ is the sample transmission, αL is the sample optical density, L_r is the CS$_2$ cell thickness, and n and n_r are the refraction indices of PDES and CS$_2$, respectively. The PDES samples were Si(Bu)$_2$ thin films cast from solution onto sapphire substrates with optical density of about 0.8.

Figure 2 shows the diffracted beam I_4 in PDES for I_3 polarized parallel to I_1, I_2 as a function of τ, for a laser intensity of 2 GW cm^{-2}; the dynamics of the optical response did not change when the laser intensity was increased by an order of magnitude. Figure 3 shows the dependence of I_4 at $\tau = 0$ on the laser intensity I ($I = I_1 + I_2 + I_3$). We find that $I_4 \sim I^{2,5}$ which is close to the theoretical I^3 dependence in DFWM experiments.[14]
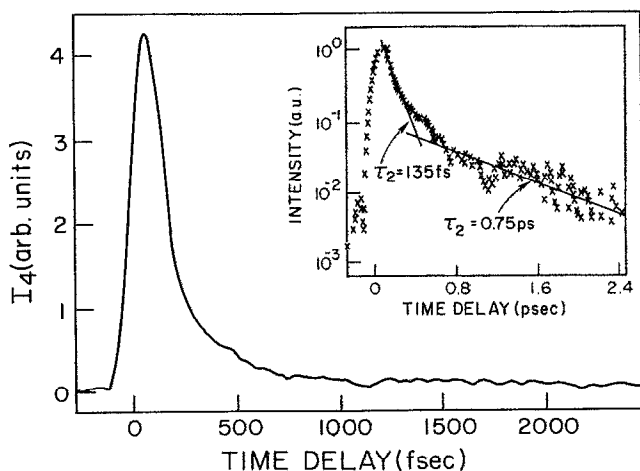

FIG. 2. Diffracted beam intensity I_4 in DFWM at 620 nm as a function of the time delay τ between the reading beam I_3 and the grating forming beams I_1, I_2. The inset is a semilog plot of I_4 (τ) showing biexponential decay.
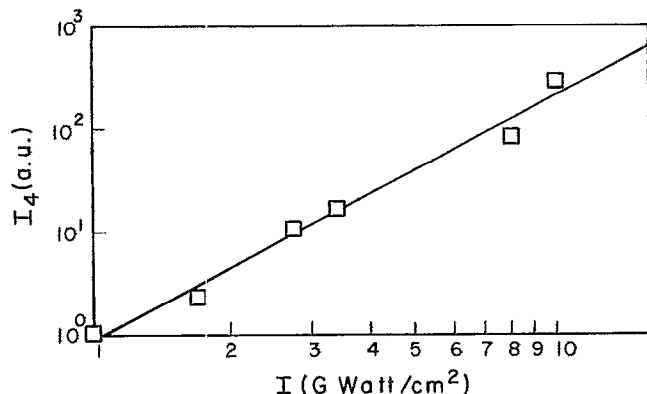

FIG. 3. Diffracted beam intensity I_4 in DFWM at $\tau = 0$ as a function of the intensity of the three other beams given in logarithmic scales; the slope is ≈ 2.5.

The reason for the small deviation in the exponent is not exactly known, but it may be due to a nonlinear dependence of α on I. From I_4 and Eq. (1) we calculate for PDES $\chi_{xxxx}^{(3)} = 3 \times 10^{-9}$ esu; the subscripts refer to the polarization of the beams I_1 to I_4. The value of $\chi^{(3)}$ was measured at 620 nm (2 eV), which is not completely in resonance with the PDES absorption band (Fig. 1). From the relation[15] $\chi^{(3)} \sim \alpha$, we anticipate $\chi^{(3)}$ to be about 10^{-8} esu at 2.2 eV (564 nm), the peak of the absorption band; this value is one of the largest ever measured for π-conjugated polymers.[2,7] We have measured $\chi^{(3)}$ at 2 eV for several conducting polymers;[7] $\chi^{(3)}$ is, for example, 6×10^{-10} esu for polythiophene, 2×10^{-10} esu for polydiacetylene 4BCMU, and 5×10^{-8} for polyacetylene.

The transient response in Fig. 2 is biexponential $Ae^{-t/\tau_1} + Be^{-t/\tau_2}$, as is more clearly shown in Fig. 2 inset, with $\tau_1 = 135$ fs and $\tau_2 = 0.75$ ps. We could not measure any long decay tail even at an order of magnitude higher laser intensity; this is in sharp contrast to polydiacetylene.[5] Our results therefore show that PDES-based devices should be able to reach a switching frequency of 0.2 THz.

The ultrafast decay component may, in principle, be due to a coherent interaction between the three beams in the DFWM technique (called coherent artifact[16]) because the three beams are derived from the same laser system. The coherent artifact can be eliminated[16,17] if the polarization of I_3 is set to be perpendicular to that of I_1 and I_2. In this case the value and dynamics of $\chi_{yxxy}^{(3)}$ is studied. We have measured I_4 in this perpendicular configuration and found no change in the dynamics of the ultrafast component; this indicates that it is not due to a coherence artifact but is a genuine intrinsic electronic process in the PDES polymer. We also found that the anisotropy in $\chi^{(3)}$ is $\chi_{yxxy}^{(3)} = \frac{1}{2}\chi_{xxxx}^{(3)}$. This deviates from the ideal anisotropy $\chi_{yxxy}^{(3)} = \frac{1}{3}\chi_{xxxx}^{(3)}$, but is in agreement with the $\chi^{(3)}$ anisotropy measured in trans-(CH)$_x$.[18]

To further study the ultrafast optical response in PDES we measured the induced transmission ΔT using the pump and probe technique with the same configuration and laser intensity as for the DFWM experiment. The transient ΔT in PDES is shown in Fig. 4; the inset shows more
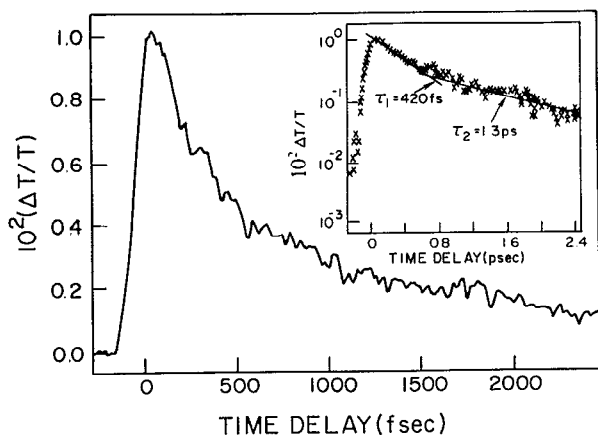
FIG. 4. Transient photoinduced transmission of PDES at 620 nm up to 2.5 ps. The inset is a semilog plot.

clearly the transient decays. Again the response is biexponential with $\tau_1 = 420$ fs and $\tau_2 = 1.3$ ps, among the fastest decays ever measured in π-conjugated polymers. To compare $\Delta T(t)$ with $I_4(t)$ we note that if I_4 in DFWM is diffracted from a real photoexcitation grating (i.e., in resonance conditions) then the two decay components of I_4 should be shorter by half compared to the two decay components of ΔT, since $I_4 \alpha (\chi^{(3)})^2$, whereas $\Delta T \alpha \chi^{(3)}$. This holds for delays $\tau > \tau_{ph}$ where τ_{ph}, is the phase memory decay constant. As seen from Figs. 2 and 4 this is true for the longer decay component in PDES since $\tau_2(I_4)$ $= \frac{1}{2} \tau_2 (\Delta T)$. However, for the short decay component $\tau_1(I_4) < \tau_1(\Delta T)$ indicating that this decay component is associated with photocarrier loss of phase memory. This may happen in PDES when photoexcited electron-hole pairs quickly renormalize into soliton-antisoliton pairs, as in trans-$(CH)_x$.[18] The slower decay component, however, is due to carrier geminate recombination[18] following the first ultrafast relaxation process. In PDES, this recombination occurs in a record time due to very efficient release of excess energy which is probably associated with the large Bu side groups, similar to polydiacetylene.[19]

In conclusion, we have discovered a novel class of π-conjugated polymers, polydiethynylsilane, with high val-

ues of $\chi^{(3)}$ in resonance conditions. PDES is soluble in various organic solvent and stable in air. Its ultrafast optical response (135 fs) is one of the fastest reported; this response and the lack of long transient tails may be exploited for optical devices in the subterahertz frequency range.

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