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Two-photon resonant third-harmonic generation in polysilanes

T. Hasegawa, Y. Iwasa, H. Kishida, and T. Koda
Department of Applied Physics, The University of Tokyo, Tokyo 113, Japan

Y. Tokura
Department of Physics, The University of Tokyo, Tokyo 113, Japan

H. Tachibana and Y. Kawabata
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

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Third-order nonlinear-optical susceptibility spectra $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ have been obtained for poly(dihexylsilane) (PDHS) and poly(dibutylsilane) (PDBS) films by third-harmonic generation (THG) measurements for a fundamental photon energy region from 1.90 to 2.15 eV, which covers the two-photon absorption (TPA) for PDHS but not for PDBS. The $|\chi^{(3)}|$ spectrum for PDHS shows a prominent peak at about 2.08 eV with a maximum value of about 2.3×10^{-12} esu, while there is no enhancement effect in PDBS in the same fundamental photon energy region. These results provide direct evidence for the two-photon-resonant THG process in polysilanes due to the one-photon-forbidden ^1A_g exciton detected by TPA and electroabsorption measurements.

In exploring fabrication of new optoelectronic materials, efforts are directed toward reducing the dimensionality of the electronic structures. In this respect, chemically synthesized semiconducting polymers may be regarded as "natural" quantum wires, whose unique properties are primarily attributed to the quantum confinement effect on the conjugated electrons delocalized in the one-dimensional (1D) polymer backbone chains.

Among such quasi-1D conjugated polymers, silicon polymers called polysilanes (PSs) are attracting considerable interest as a model system for a 1D version of tetrahedrally coordinated silicon crystals.[1] Among several interesting features of PS's, the third-order nonlinear-optical (NLO) properties have been investigated by many researchers, after work by Kajzar, Messier, and Rosilio.[2] As a result, it has been revealed that there is a dipole-forbidden (^1A_g) excited state about 0.8–0.9 eV above the lowest dipole-allowed exciton state. Experimentally, the ^1A_g state has been detected by two-photon absorption[3–5] (TPA). Recently, electroabsorption (EA) measurements have been made on PS films,[6] and have revealed a field-induced feature at an energy almost coincident with the TPA peak (cf. Fig. 2 in Ref. 6). It has been suggested that the same ^1A_g exciton state is responsible for both the TPA and EA peaks. Much work has been done both experimentally and theoretically with regard to the role of the dipole-forbidden ^1A_g excited state located higher than the lowest dipole-allowed ^1B_u exciton state in the third-order NLO process in PS's and other conjugated polymers as well.[7–10] In view of the controversial situation, it will be useful to examine if the ^1A_g exciton detected by TPA and EA measurements as described above is involved in the third-harmonic generation (THG) process. The aim of this paper is to answer this question by presenting experimental evidence for such a TP resonant enhancement of the THG process in PS films.

For this purpose, we selected two specific kinds of poly(dialkylsilanes) $(-\mathrm{Si}RR'-)_n$ one with *n*-hexyl chains ($R=R'=C_6H_{13}$) and the other with *n*-butyl chains ($R=R'=C_4H_9$) as the substitutional side groups, R and R'. They are abbreviated as PDHS [poly(dihexylsilane)] and PDBS [poly(dibutylsilane)], respectively. The former polymer has an all-*trans*-planar backbone structure, while the latter has a 7/3 helical backbone structure.[1,6]

In the experiments, powder samples of PDHS and PDBS were synthesized by a method described elsewhere.[5,6] The distribution of molecular weights of the polymers was measured by a polystyrene calibration method. It turned out that the molecular weight distribution was monomodal, centered at about 2.44×10^5 for both PS's. These polymers were dissolved in heptane and were spin coated onto silica plates to form thin unoriented films of about 0.15 μm in thickness. The films were dried at 380 K for 15 min and allowed to stand at room temperature overnight, before optical measurements. Films fabricated in this way show exciton absorption spectra which are considerably sharper than spectra reported before. All optical measurements were made at room temperature.

The ordinary one-photon absorption (OPA) and the TPA spectra of PDHS and PDBS films are shown in Fig. 1. The TPA spectra were measured by monitoring the intensities of luminescence as a function of the photon energy of exciting laser light, as described before.[5] Observed luminescence intensities were corrected for the two-photon excitation intensities, and were plotted against the two-photon energy to compare with the OPA spectrum. From these results, energies of the dipole-forbidden ^1A_g exciton levels at room temperature are determined to be 4.19 ± 0.02 eV for PDHS and 4.76 ± 0.02 eV for PDBS, respectively. The EA measurements were also made on PDHS and PDBS films by the experimental procedure as described earlier.[6] The result for PDHS film will be shown later in Fig. 3 in comparison with the TPA spectra. The energy-level diagrams deduced from the OPA, TPA, and EA data are shown in the insets in Fig. 1.

For the measurement of THG, sample films were irra-

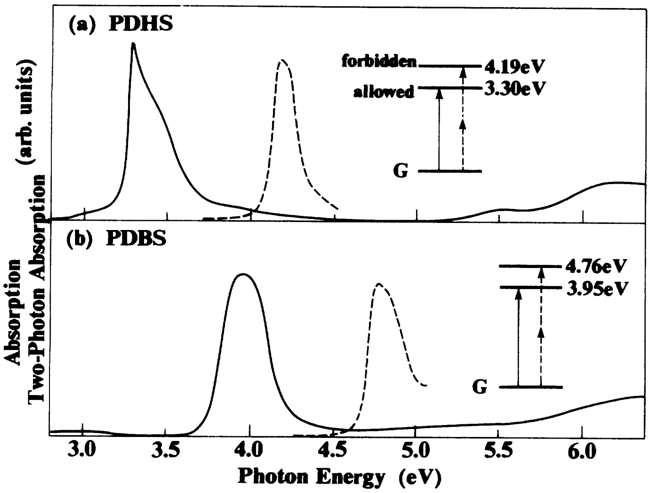

FIG. 1. Ordinary one-photon absorption spectra (solid lines) and two-photon absorption spectra (dashed lines plotted against the two-photon energy) of (a) poly(dihexylsilane) (PDHS) film and (b) poly(dibutylsilane) (PDBS) film at room temperature. The insets show energy-level schemes for respective polysilanes deduced from these spectra.

diated from the spin-coated side with 15-ns-wide laser pulses from a dye laser (LAMBDA PHYSIK FL2002) driven by a 308-nm Xe-Cl excimer laser (LAMBDA PHYSIK EMG53MSC). Using suitable dyes (rhodamine 6G, *B*, and 101), the photon energy of the laser light was scanned over a region from 1.90 to 2.15 eV. Note that this photon energy region covers the TPA peak in PDHS, but not in PDBS for which the photon energies used are far below the TPA band.

A standard Maker fringe method[2,11] was employed to evaluate the values of $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ as a function of fundamental photon energy $\hbar\omega$. Samples were placed in a vacuum chamber to avoid the appreciable air contribution to observed third-harmonic intensities of a silica plate used as a standard. The ultraviolet (uv) third-harmonic light was separated from the fundamental laser light and the sample luminescence by using a uv bandpass filter and a monochromator. The third-harmonic lights were detected by a solar-blind photomultiplier tube, and were processed by a boxcar averager. Figure 2 shows a typical example of the Maker fringe pattern, that is the third-harmonic intensities as a function of the incident angle of the fundamental laser beam impinging upon the sample film, for a 0.152-μm-thick PDHS film, together with the pattern for a 300-μm-thick silica plate as a standard, both for the fundamental light at 2.05 eV. The silica plate is transparent up to 7.3 eV in the uv region.

The power dependence of third-harmonic intensities was measured on PDHS and PDBS films, and also on the silica plate. A cubic dependence was observed over 2 orders of magnitude, indicating that there was no saturation effect nor thermal interference effect on the observed third-harmonic intensities. In order to prevent PS films from TP-induced degradation effect,[12] the laser power densities on the PS films were kept below the maximum level of a few MW/cm^2. For the same precaution, each measurement at a fixed fundamental photon energy was made at a fresh spot on the sample film.

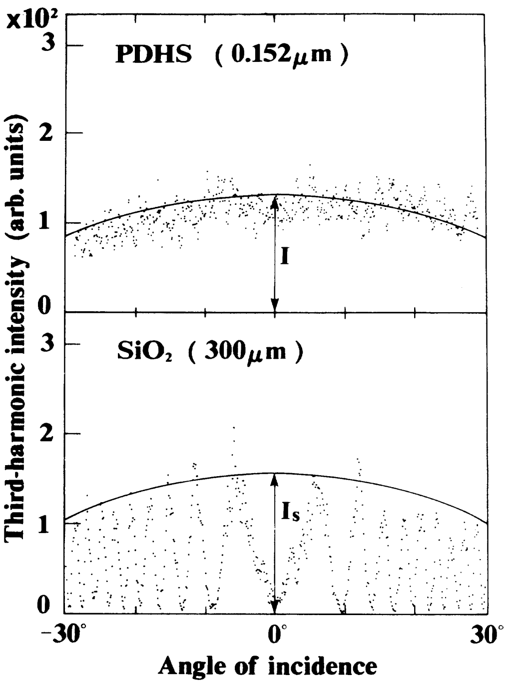

FIG. 2. Typical third-harmonic intensity patterns for a 0.152-μm-thick poly(dihexylsilane) (PDHS) film on a silica plate (upper) and for a 300-μm-thick silica plate (lower), both at the fundamental photon energy of 2.05 eV, as a function of incidence angle of the fundamental pulse laser light to the sample.

Experimental values for $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ represent the modulus of spatially averaged $\gamma_{XXXX}(-3\omega;\omega,\omega,\omega)$ component for polymers randomly oriented in the film. These values were evaluated from observed third-harmonic intensities for the sample, I, and of a silica plate, I_s (see Fig. 2), by using the following relation,[11]

$$|\chi^{(3)}| = \frac{2}{\pi}\left(\frac{I}{I_s}\right)^{1/2}\frac{l_{c,s}}{l}|\chi_s^{(3)}| . \tag{1}$$

Here, l is the thickness of PS film, and $l_{c,s}$ is the coherence length of the silica plate. The values of third-order nonlinear-optical susceptibility of silica, $\chi_s^{(3)}$, were estimated at various fundamental photon energies, from the literature value measured at fundamental wavelength of 1.907 μm, taking account of the dispersion by using Miller's rule, $\delta = \chi_s^{(3)}(-3\omega;\omega,\omega,\omega)/\chi_s^{(1)}(\omega)^3\chi_s^{(1)}(3\omega)$ being constant.[13] Experimental results for $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ values of PDHS and PDBS films are plotted in the lower part of Fig. 3 against the fundamental photon energy.

It is readily seen in this figure that the $|\chi^{(3)}|$ spectrum for PDHS shows a clear maximum at about 2.08 eV, the double of which is very close to the TPA and EA peaks shown on the upper part of Fig. 3. The maximum $|\chi^{(3)}|$ value for PDHS is about 2.3×10^{-12} esu. It seems that a resonant enhancement of about 1.5×10^{-12} esu at the peak is superposed on a broad background due to the

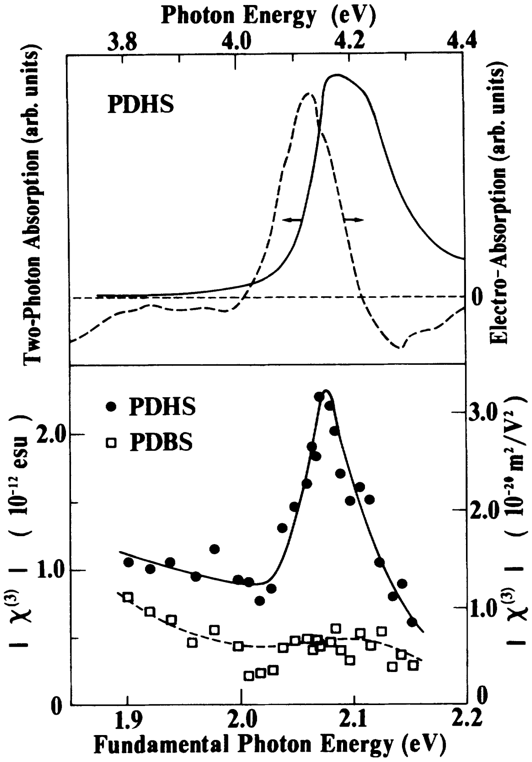

FIG. 3. Third-order nonlinear optical susceptibility $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of poly(dihexylsilane) (PDHS) films (solid circles with a solid line as a guide for eye) and of poly(dibutylsilane) (PDBS) films (open squares with a dashed line as a guide for eye) at room temperature. The fundamental photon energy of the pumping laser beam is shown in the lower abscissa. In the upper part, the two-photon absorption spectrum (solid line) and electroabsorption spectrum (dashed line) of PDHS film are plotted against two-photon energy in the upper abscissa.

non-TP-resonant contribution of the order of 1×10^{-12} esu. In contrast, in the $|\chi^{(3)}|$ spectrum for PDBS, no sign of enhancement effect is seen in the same photon energy region. This is just as expected, since the dipole-forbidden exciton state detected by the TPA (and EA) measurements in PDBS is located at about 4.76 eV, as shown in the inset in Fig. 1, which is far beyond the TP resonance limit in the present THG measurement. Experimental results presented above clearly demonstrate that the dipole-forbidden ^1A_g exciton detected by TPA and EA measurements in PDHS is definitely involved in the two-photon-resonant THG process. This is direct evidence for the two-photon-resonant THG enhancement effect due to the higher-lying ^1A_g exciton in a 1D polymeric system.

As for carbon-based π-conjugated polymers, the TP-resonant enhancement effect on THG has been investigated on polyacetylene,[14] polydiacetylene,[15] and polythiophene.[7] For polyacetylene, it has been argued that the TP-resonant THG enhancement occurs at about half of the band gap,[14] though theoretical interpretation is not well established as yet. In polydiacetylene and polythiophene, experimental features in the $|\chi^{(3)}|$ spectra have been attributed to an optically forbidden ^1A_g state which is located just below the ^1B_u exciton energy. However, possible participation of higher-lying ^1A_g state in these π-conjugated polymers has not been subject to experimental investigation so far. In contrast, in the present study we were able to observe the TP-resonant THG process in PS's which is evidently attributable to an ^1A_g state which is located above the lowest ^1B_u exciton state. This interpretation is supported by other two kinds of NLO effect, TPA and EA, providing the first convincing evidence for the contribution of the higher-lying ^1A_g state in the 1D polymeric systems. We suggest that similar TP-resonance effect is likely to be observed in polydiacetylenes too, since EA spectra[16] and electroreflectance (ER) spectra[17,18] for polydiacetylene show a field-induced feature which is very similar to the ^1A_g exciton-related feature in the EA spectra of PS's.

The features appearing in the TPA, EA, and THG spectra for PDHS, as seen in Fig. 3, are located very close to each other, indicating that the same dipole-forbidden ^1A_g exciton state is responsible for these features. But it is also noticed that the spectra as a whole exhibit considerably different shapes in the two-photon-resonance region. These spectral shapes can be analyzed in terms of different third-order NLO processes represented by $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for THG, $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ for TPA, and $\chi^{(3)}(-\omega;0,0,\omega)$ for EA. A detailed spectral analysis of these experimental NLO spectra is left to a forthcoming paper, and we shall make only the following remarks.

First, we note that the $|\chi^{(3)}|$ spectrum for PDHS shows a sharp peak at around 2.08 eV, whereas the TPA spectrum is considerably broader with a tail extending to the higher-energy side. (Similar features are also seen in the three-photon-resonant $|\chi^{(3)}|$ and OPA spectra in polydiacetylenes.[16,19]) Qualitatively, this difference seems to be attributable to the fact the THG spectrum is related with the modulus $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$, whereas the TPA spectrum is associated with $\mathrm{Im}\chi^{(3)}(-\omega;\omega,\omega,-\omega)$.

Second, it is noticed that the EA spectrum shows a peak located slightly lower than the peaks of the THG and TPA spectra. In addition, there is a broad negative peak at around 4.29 eV. Such a feature has also been observed in the EA spectra of many PS's (Ref. 6) (and also in the ER spectra of polydiacetylenes[17,18]). For the explanation of this negative peak, it is necessary to assume that a weak one-photon allowed state exists on the high-energy side of the ^1A_g exciton. This one-photon allowed state may be related to the second dipole-allowed exciton or else the band-gap states as suggested by Abe *et al.*[20]

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