Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nonlinear Optical Properties of Polysilanes

Tatsuo Hasegawa [a], Yoshihiro Iwasa [a], Hideo Kishida [a], Takao Koda [a], Yoshinori Tokura [b], Hiroaki Taceibana [c] & Yasujiro Kawabata [c]

[a] Department of Applied Physics, The University of Tokyo, Tokyo, 113, Japan

[b] Department of Physics, The University of Tokyo, Tokyo, 113, Japan

[c] National Chemical Laboratory for Industry, Tsukuba, Ibaraki, 305, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Tatsuo Hasegawa , Yoshihiro Iwasa , Hideo Kishida , Takao Koda , Yoshinori Tokura , Hiroaki Taceibana & Yasujiro Kawabata (1992): Nonlinear Optical Properties of Polysilanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 25-30

To link to this article: http://dx.doi.org/10.1080/10587259208046871

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 25–30
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

NONLINEAR OPTICAL PROPERTIES OF POLYSILANES

TATSUO HASEGAWA, YOSHIHIRO IWASA, HIDEO KISHIDA, and TAKAO KODA
Department of Applied Physics, The University of Tokyo, Tokyo 113, Japan

YOSHINORI TOKURA
Department of Physics, The University of Tokyo, Tokyo 113, Japan

HIROAKI TACHIBANA and YASUJIRO KAWABATA
National Chemical Laboratory for Industry, Tsukuba , Ibaraki 305, Japan

Abstract We have measured a spectrum of third-order nonlinear optical susceptibility $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of a σ-conjugated polysilane, poly(di-n-hexylsilane) (PDHS), by means of third-harmonic generation (THG) measurement, in the fundamental photon energy region from 0.56 eV to 2.15 eV. The obtained $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectrum exhibits three peaks. These peaks are interpreted as the multi-photon resonance enhancement to the one-dimensional exciton states. This exciton model can be applied also to the nonlinear optical response of other conjugated polymers.

INTRODUCTION

Among various "unconventional" photo-active molecular systems under current interest, silicon-based polymers, called polysilanes (PS's), are attracting considerable interest.[1] The major reason is that PS's have the largest third-order nonlinear optical (NLO) susceptibility among colorless materials.[1-4] In addition to these remarkable NLO properties, processability by various chemical modification of side-groups of the polymer makes PS's quite attractive for future NLO applications.

As for the linear and nonlinear optical properties of PS's, it has been almost recognized that exciton states are playing essential roles.[5] In the quasi one-dimensional (1D) system as PS's, the excitonic effect becomes significant as compared with the three-dimensional (3D) system as crystalline silicon. In this sense, PS's can be regarded as an assembly of "natural quantum wires" which

realizes the 1D exciton states. However, detailed understanding of the exciton effects in the NLO processes is not complete as yet.

In this paper, we present the results of NLO study on PS's. We have measured the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectrum of poly(di-n-hexylsilane) (PDHS) by means of third-harmonic generation measurement over as wide fundamental photon energy region as possible. Our major interest is in the multi-photon resonance effect observed in the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectrum. We will discuss these results in terms of the 1D excitonic resonances in PS's. A part of this work has been published elsewhere.[6]

EXPERIMENTAL

We have studied poly(di-n-hexylsilane) $(-Si(C_6H_{13})_2-)_n$ (abbreviated as PDHS), which is known to have an all-trans planar backbone structure, having a center of symmetry, at room temperature. One-photon, two-photon, and electro-modulated absorption spectra were measured on the spin-coated film of PDHS following the procedure described before.[4-7] From these spectra, the lowest optically allowed exciton (1^1B_{1u} exciton) level is located at about 3.30eV, and the second optically forbidden exciton (^1A_g exciton) level is located at about 4.19eV, respectively at room temperature. Schematic energy level diagram of these exciton states will be shown later (Fig.4).

Measurements of third-harmonic generation (THG) were made on the PDHS films (about 150nm thick) on top of a silica substrate. Fundamental laser beam (photon energy region from 0.56eV to 2.15eV) was obtained, using three kinds of laser systems, details of which were described elsewhere.[6,8] The obtained laser beam was focused on the sample, using a 10cm focal length lens. Samples were placed in a vacuum cell to avoid the effect of air.

To evaluate the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of PDHS, we used the standard Maker fringe technique.[8] We used the fused synthetic silica plate as a standard of $|\chi^{(3)}|$. At first, laser power dependence of the third-harmonic intensities were measured on the PDHS films and also on the standard silica plate (Fig.1). As shown in Fig.1, they obey third-power dependence fairly well within our used power densities (a few MW/cm^2), indicating that there was no saturation on

the observed third-harmonic intensities. Examples of the third-harmonic intensity patterns of (a) the PDHS film and of (b) the silica plate, as a function of the incidence angle, are shown in Fig.2. As shown in the Fig.2.(a), a monotonously decreasing pattern is observed in the third-harmonic intensity pattern of the PDHS film, since the film thickness l is much shorter than the coherence length of THG in PDHS. In this case, experimental values for $|\chi^{(3)}|$ were evaluated from observed third-harmonic intensities of the PDHS film (I) and of the standard silica plate (I_S) (see Fig.2), by using the following expression;

$$|\chi^{(3)}| = \frac{2}{\pi} \cdot \sqrt{\frac{I}{I_s}} \cdot \frac{l_{c,s}}{l} \cdot |\chi_s^{(3)}| \qquad (1)$$

Here, $|\chi_s^{(3)}|$, $l_{c,s}$ are the third-order nonlinear optical susceptibility and the coherence length of the standard synthetic fused silica, respectively. The spectra of these values, which are plotted in Fig.3, were calculated from the dispersion relation of refractive index of this silica plate and the Miller's rule.[9]

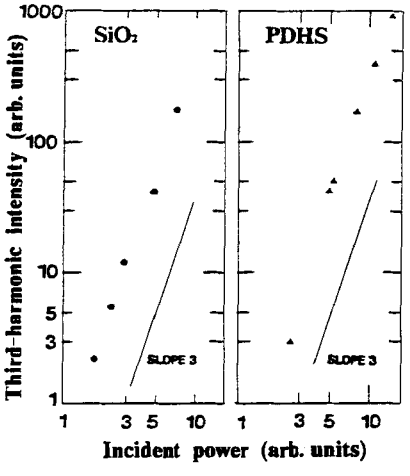

FIG.1 Fundamental laser power dependence of third-harmonic intensities from the standard silica plate and the PDHS film at photon energy of 2.05eV. Solid lines show the third-power law.

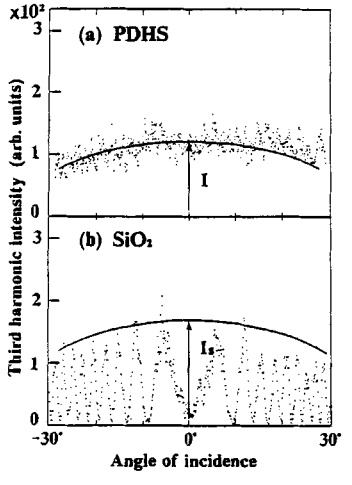

FIG.2 Third-harmonic intensity patterns of (a) PDHS film with a thickness of 152nm and (b) standard synthetic fused silica plate (0.3mm) as a function of incidence angle.

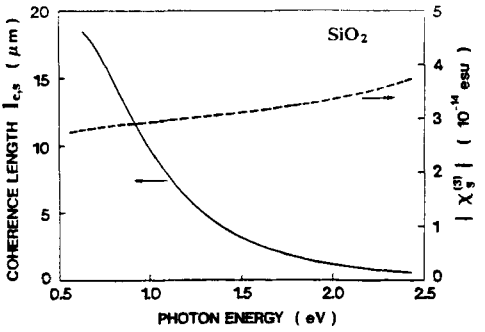

FIG.3 $|\chi_s^{(3)}|$, and $l_{c,s}$ of the synthetic fused silica plate used as a standard.

RESULTS AND DISCUSSIONS

The experimentally obtained $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ values are plotted as a function of fundamental photon energy in Fig.4. There are three major structures, denoted A, B, and C at about 1.15eV, 1.5eV, and 2.1eV, respectively. We will discuss the origin of these structures, based upon the schematic energy level diagrams in the lower part of Fig.4, which is obtained by one-photon, two-photon, and electro-modulated absorption spectra. We could not obtain the data points from 0.8eV to 1.1eV, because a suitable laser system was unavailable.

The structure A located at 1.15 eV shows the largest $|\chi^{(3)}|$ value. This energy is very close to the one-third of the one-photon absorption peak energy at about 3.30 eV. Therefore, the structure A is attributed an enhancement effect due to a three-photon resonance process to the lowest allowed 1^1B_{1u} exciton level, as shown in the diagram of Fig.4. Similar three-photon resonance effects have been reported elsewhere.[4] The internal attenuation effect of the third-harmonic radiation in the film is not considered.

Next, we will discuss the origin of the structure C, which exhibits the small peak located at about 2.1 eV. This energy is very close to the half of the ^1A_g exciton energy (diagram of Fig.4). This exciton is one-photon forbidden in the centrosymmetric (C_{2h} symmetry) backbone of PDHS. Therefore, it is detected only by the two-photon absorption or electro-absorption spectra. The structure C can be understood as a two-photon resonance peak to this ^1A_g exciton level. Lastly, we will discuss about the structure B, which is located at

about 1.5 eV. As for the structure B, we propose an interpretation in terms of a three-photon resonance enhancement to a higher-lying allowed state (which has a $^1B_{1u}$ symmetry) at around 4.5eV (diagram in Fig.4). This higher-lying state can be assigned to the third-exciton or the band-edge in PDHS. It should be noted here that this model agrees well with the electro-absorption spectrum.

The energy level diagram shown in Fig.4 has a wide applicability for nonlinear optical response of 1D semiconductors, such as conjugated polymers. As in the 1D semiconductors the excitonic effect is significantly strong, the excited states are composed of discontinuous exciton levels which have "anomalously" large binding energy (~1eV), and the band-to-band absorption becomes rather weak.[10,11] In the 1D Wannier-like exciton model, the 1^1B_{1u} exciton, ^1A_g exciton, and 2^1B_{1u} exciton correspond to the n=1, 2, 3 excitons, respectively.

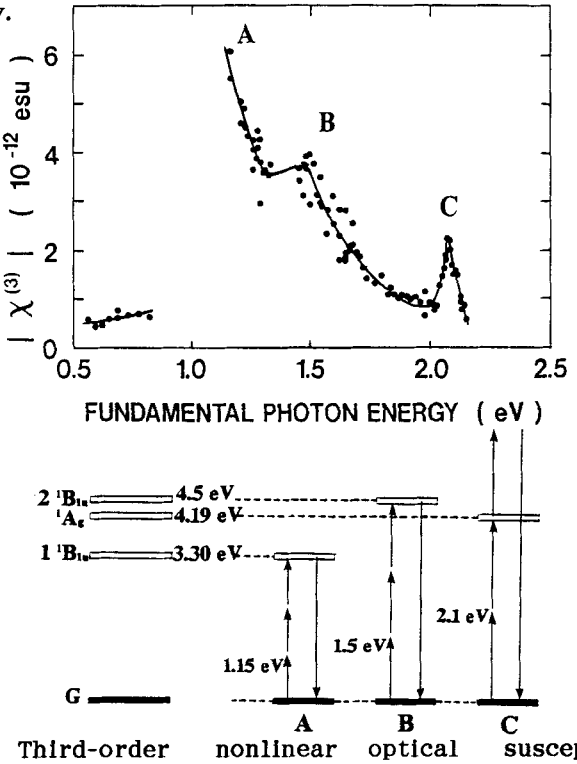

FIG4 Third-order nonlinear optical susceptibility $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of poly(di-n-hexylsilane) (PDHS) films as a function of fundamental photon energy. Filled circles are experimental points, and a solid line is a guide for eye. A schematic energy level diagram and NLO processes are shown in the lower part.

In conclusion, the $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ spectrum of PDHS has revealed three peaks. They are attributable to the multi-photon resonance enhancement to the 1D exciton states, which are considered to be fairly common in an extended 1D systems.

ACKNOWLEDGMENTS

We are grateful to Drs. H.Kobayashi and K.Kubodera, and Prof. K.Miyano for their help in the THG measurement. This study was supported in part by a Research-Grant-in-Aid from the Ministry of Education, Culture and Science in Japan, the Nissan Science Foundation, and the NEDO foundation, Japan.

References

1. R.D.Miller and J.Michl, Chem. Rev., 89 (1989) 1359, and reference therein.
2. F.Kajzar, J.Messier, and C.Rosilio, J. Appl. Phys., 60 (1986) 3040.
3. J.-C.Baumert, G.C.Bjorklund, D.H.Jundt, M.C.Jurich, H.Looser, R.D.Miller, J.Rabolt, R.Sooriyakumaran, J.D.Swalen, and R.J.Twieg, Appl. Phys. Lett., 53 (1988) 1147.
4. J.R.G.Thorne, J.M.Zeigler, and R.M.Hochstrasser, in "Long Scale Molecular Systems" ed. By W.Gans, Plenum NY 1991.
5. H.Tachibana, Y.Kawabata, S.Koshihara, and Y.Tokura, Solid State Commun., 75 (1990) 5.
6. T.Hasegawa, Y.Iwasa, H.Kishida, T.Koda, Y.Tokura, H.Tachibana, and Y.Kawabata, to be published in Phys. Rev. B.
7. Y.Moritomo, Y.Tokura, H.Tachibana, Y.Kawabata, and R.Miller, Phys. Rev. B (in press).
8. K.Kubodera and H.Kobayashi, Mol. Cryst. Liq. Cryst. 182A (1990) 103.
9. F.Kajzar and J.Messier, Phys. Rev. A32 (1985) 2352.
10. R.Loudon, Amer. J. Phys. 27 (1959) 649.
11. T.Ogawa and T.Takagahara, Phys. Rev. B43 (1991) 14325.