Photodegradation of Polysilane Polymers by Nonresonant Two-Photon Excitation

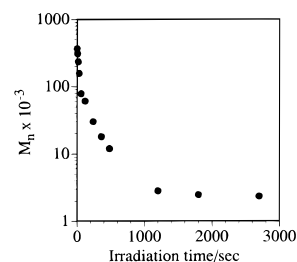Takashi Miyazawa,[†] Titao Saeki,[‡] Chengyou Liu,[†] and Mitsuo Kira*,[†,‡]

*Photodynamics Research Center, The Institute
of Physical and Chemical Research (RIKEN)
19-1399, Koeji, Aoba-ku, Sendai, 980, Japan
Department of Chemistry, Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-77, Japan*

Linear polysilanes with effective σ-conjugation are known to have distinct low-lying two-photon allowed excited states (2^1A_g states),[1] resembling π-conjugated linear polyenes. During the course of our studies of selective photoreactions induced by nonresonant two-photon (NRTP) excitation,[2] we have discovered that photodegradation mode of a linear peralkylpolysilane polymer via the NRTP excitation is quite different from that through the conventional single-photon (SP) excitation. Photoreactions of polysilanes using SP excitation have been extensively studied.[3] Typically, exhaustive SP irradiation of poly(dihexylsilylene) (PDHS) with 254 nm (CW) or 248 nm (pulsed) light in the presence of triethylsilane gives silylene-trapping products Et_3-$SiSiR_2H$ (R = hexyl) and the homolytic cleavage products $H(SiR_2)_nH$ (n = 2, 3),[3e,f] while the final length of the silicon chain depends on the wavelength of the light used.[4] In contrast, the NRTP excitation of PDHS induces selective formation of medium-chain oligosilanes containing ca. 10 silicon atoms irrespective of the irradiation wavelength, probably due to the size effect of the optical nonlinearity or the two-photon absorption coefficient.[5,6]

Irradiation of a hexane solution of PDHS (2.0 g/L, M_n = 366 000, M_w/M_n = 1.23)[7] using 532 nm laser pulses (the second

† RIKEN.
‡ Tokohu University.
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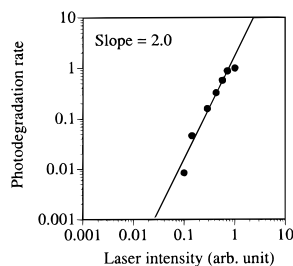(2) (a) Kira, M.; Miyazawa, T.; Koshihara, S.; Segawa, Y.; Sakurai, H. *Chem. Lett.* **1995**, 3. (b) Miyazawa, T.; Koshihara, S.; Segawa, Y.; Kira, M. *Chem. Lett.* **1995**, 217. (c) Miyazawa, T.; Liu, Z.; Liu, C.; Koshihara, S.; Kira, M. *Chem. Lett.* **1996**, 1023. (d) Miyazawa, T.; Liu, C.; Kira, M. *Chem. Lett.* **1997**, 459. (e) Miyazawa, T.; Liu, C.; Koshihara, S.; Kira, M. *Photochem. Photobiol.* **1997**, *66*, 566.
(3) (a) West. R. *J. Organomet. Chem.* **1986**, *300*, 327 and references therein. (b) Miller, R. D. In *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; American Chemical Society: Washington, DC, 1989; p 413. (c) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (d) Michl, J.; Downing, J. W.; Karatsu, T.; Mckinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959. (e) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737. (f) Karatsu, T.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1140. (g) McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Thompson, D. P.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 2003. (h) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett.* **1983**, *21*, 823.
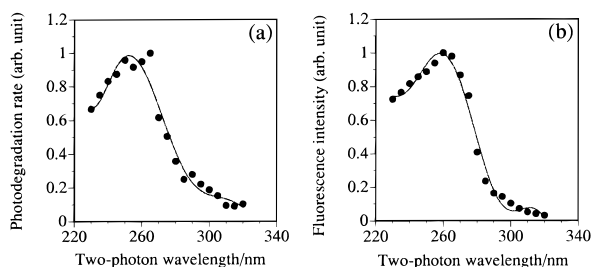(4) Products such as $H(SiR_2)_nH$ (n = 2, 3) are not formed either upon irradiation at >300 nm because linear peralkyloligosilanes with the chain length less than 7 are transparent.[3f]
(5) Abe, S. In *Light Emission from Novel Silicon Materials*; Kamimura, H., Kanemitsu, Y., Kondo, M., Takeda, K., Eds.; The Physical Society of Japan: Tokyo, 1994; p 56.
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Figure 1. Time course of M_n of PDHS during irradiation with 532 nm laser pulses (100 mJ/pulse, 10 Hz).

harmonic of a Nd:YAG laser, pulse duration ∼6 ns, 100 mJ/pulse, 10 Hz)[8] induced facile photodegradation as shown in Figure 1. The averaged molecular weights decreased rapidly with increasing irradiation time but the degradation rate strikingly slowed at M_n = ca. 2500 and converged to ca. 2000 after 45 min of irradiation (M_w/M_n = 1.32). The final products were assigned as a mixture of oligo(dihexylsilylene)s with ca. 10 silicon atoms on the basis of the UV−vis, IR, and ^1H, ^{13}C, and ^{29}Si NMR spectra, while the terminal substituents could not be determined spectroscopically.[9a] The absorption maximum at room temperature is found at around 290 nm, which is very close to that of perhexyldecasilane.[9b] The NRTP irradiation of PDHS in the presence of excess triethylsilane or ethanol with 532 nm laser pulses have failed to trap silylenes, i.e., no silylene extrusion occurs during the NRTP irradiation.

The photodegradation rates were determined by monitoring M_n as a function of the irradiation time (t). If we assume no cross-linking occurs during the photodegradation of PDHS, the time-dependence of M_n is represented by eq 1, where M_n^0 is the initial number-averaged molecular weight and k_{app} is an apparent rate constant, which depends on the two-photon absorption efficiency, the quantum efficiency for the scission, and the laser intensity. As expected, a good linear relationship was obtained between $1/M_n$ and t, when the irradiation wavelength and power were both constant.[10]

$$\frac{1}{M_n} = \frac{1}{M_n^0} + k_{app}t \qquad (1)$$

The two-photon nature of the photodegradation of PDHS using 532 nm pulsed laser was evidenced by the following experiments: (1) the power and the wavelength dependence of the photodegradation rates of PDHS and (2) a photoreaction of PDHS with CW 514 nm from Ar^+ laser. As expected, the apparent rate

(7) Poly(dihexylsilylene) was prepared using a modified Wurtz coupling of dichlorodihexylsilane with sodium metal in dry octane.[3a,c] Molecular weight distribution was determined relative to polystyrene standards using a JAI model LC908 GPC instrument with a series of a JAIGEL AC-80M and a Shodex AC-804 columns.
(8) There is no SP absorption band of PDHS at around 532 nm, while the two-photon absorption maximum appears at around 260 nm at room temperature in solution.[1]
(9) (a) UV−vis, IR, and NMR spectra as well as the GPC profile of the product mixture are given in the Supporting Information. (b) The following absorption maxima (ϵ in parentheses) were observed for some perhexyloligosilanes: 290 nm (50 000) and 281 nm (41 000) for $Si_{10}Hex_{22}$ and Si_8-Hex_{18}, respectively (Obata, K.; Kira, M. To be published). The yield of an isolated mixture of oligosilanes was estimated as 30% by assuming the apparent ϵ is the same as that for $Si_{10}Hex_{22}$.
(10) A similar equation is derived to the weight-averaged molecular weight M_w: $1/M_w = 1/M_w^0 + k_{app}'t$.[11] The k_{app}/k_{app}' value observed in our experiments was ca. 1.5, which gave no meaningful value for the cross-linking quantum yield. No serious cross-linking has been found for SP degradation of poly-(di-n-alkylsilylene) in solution.[3h]
(11) (a) Kilb, R. W. *J. Phys. Chem.* **1959**, *63*, 1838. (b) Wilson, C. G. In *Introduction to Microlithography*; Wilson, C. G., Bowden, M. J., Eds.; ACS Symposium Series 219; American Chemical Society: Washington, DC, 1983; Chapter 3 and references therein.
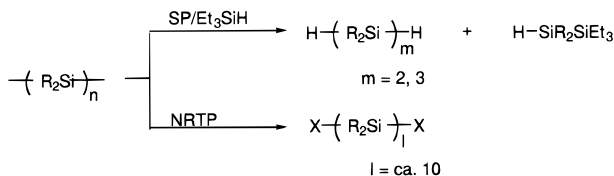
Figure 2. Square dependence of the apparent rate constants of the photodegradation of PDHS in hexane on the incident laser intensity (532 nm).

Figure 3. Plots of (a) apparent rate constants of photodegradation of PDHS in hexane and (b) relative fluorescence intensity of PDHS monitored at 350 nm, against a half of the incident laser wavelengths.

Scheme 1

constant k_{app} of PDHS in hexane increased in proportion to the square of the laser intensity at 532 nm as shown in Figure 2. The dependence of k_{app} on the excitation wavelengths (λ_{ex}) was investigated between 460 and 640 nm (10 mJ/pulse, pulse duration ∼3 ns, 10 Hz).[12] The action spectrum showed a maximum at around $\lambda_{ex} = 520$ nm as shown in Figure 3a, being good in agreement with the two-photon absorption spectrum (Figure 3b) obtained by the two-photon fluorescence (TPF) method, where the $S_1 \rightarrow S_0$ fluorescence intensity at 350 nm showed the maximum at the same wavelength of the incident laser light. The ratio of the NRTP photodegradation rates of PDHS excited by circularly and linearly polarized lights (I_c/I_l) in a room-temperature solution was found to be 0.80 ± 0.15, which is good in accord with that observed for the NRTP absorption intensity using the TPF method,[13] indicating that the ground-state and the excited-state wave functions have the same symmetry in the point group.

When a hexane solution of PDHS was irradiated with CW 514 nm light (1 W) from Ar$^+$ laser, the photodegradation rate was ca. 4000 times smaller compared to that induced by the 532 nm

laser pulses (100 mJ/pulse, 10 Hz), even though the integrated intensity for the former irradiation was identical with the latter.[14] The results indicate that the photodegradation induced by the laser pulses is caused by neither heat-up of the sample nor a very weak linear singlet−triplet absorption.

Several aspects merit specific comment. The observed two-photon nature of the photodegradation of polysilanes does not mean that the excited state responsible for the photoreactions is the two-photon excited state. In reality, the lowest singlet state (^1B_u state) reached via the facile internal conversion from the two-photon state would be responsible for the photodegradation of a polysilane because the photochemical behavior via the NRTP excitation is closely related to that via the SP excitation. The fact that the NRTP degradation of PDHS does not give the corresponding silylene is compatible with the proposed view[3f] that only excitation of the shorter chromophores in the polymer chain up to perhaps Si$_7$ or so causes silylene extrusion, while excitation of the longer ones does not.

The nature of the two-photon excited states of short-to-medium-chain oligosilanes has recently attracted much attention both experimentally and theoretically, in relation to the confinement of the excited states or the size effect of optical properties of one-dimensional electronic systems.[5,6,15] Using electroabsorption spectroscopy, the two-photon absorption band of linear Si$_{10}$Me$_{22}$ has been found at around 5.32 eV,[6] which is 1.15 eV higher in energy than that of PDHS[1] and corresponds to the two-photon absorption maximum of 233 nm, with much lower signal intensity than that for PDHS.[6] The magnitude of the third-order nonlinear optical susceptibility $\chi^{(3)}$, whose imaginary part is proportional to the two-photon absorption coefficient, has also been shown by calculations using Sandorfy-C-PPP model to depend remarkably on the chain length.[5] The inertness of the medium-chain oligosilanes upon the NRTP irradiation is not explained by the transparency of the oligosilanes at 532 nm, because the degradation profile of PDHS using 470-nm laser pulses was mostly the same as that shown in Figure 1. The major reason for the inertness of the medium-chain oligosilanes upon the NRTP irradiation can be ascribed to the substantial difference of the exciton nature between the oligosilanes and polysilanes, i.e., a very low two-photon absorption coefficient of the oligosilanes compared with the long-chain oligosilanes or polysilane segments having at least 10−20 silicon chain lengths as suggested by the segment model of the polysilane chromophore.[15,16]

In conclusion, the NRTP excitation of poly(dihexylsilylene) induces facile photodegradation to yield medium-chain oligosilanes containing ca. 10 silicon atoms, being indicative of substantial difference of the two-photon excited-state nature between the medium-chain oligosilanes and long-chain polysilanes.

Supporting Information Available: UV−vis, IR, and various NMR spectra and GPC charts of the NRTP photodegradation products of poly-(dihexylsilylene) (5 pages). See any current masthead page for ordering information and Internet access instructions.

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(12) The variable-wavelength pulsed lights were generated with an optical parametric oscillator (Spectra Physics MOPO 710), which was pumped by the third harmonic of a pulsed Nd:YAG laser (Spectra Physics GCR 250−10).

(13) The I_c/I_l value for PDHS in methylcyclohexane has been reported to be 0.65 ± 0.3 over the range of 660−532 nm by the TPF method, being good in accord with the theoretical prediction.[1a]

(14) Because spatial and time profile of the laser beam is different between the two experiments, the quantitative meaning should not be expected from the factor observed here.

(15) Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265 and references cited in.

(16) The two-photon absorption maxima for the produced oligo(dihexylsilylene)s are assumed here to be similar with the maximum for Si$_{10}$Me$_{22}$.[6]