Photodegradation of Alkyl- and Aryl-Substituted Polysilanes Studied by Flash Photolysis

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ABSTRACT: The photodegradation of poly(cyclohexylmethylsilane) and poly(phenylmethylsilane) was investigated by flash photolysis and quenching experiments. The time-resolved absorption spectra of poly(cyclohexylmethylsilane) showed a sharp transient absorption peak at 370 nm with an absorption shoulder near 430 nm. These transient absorption bands were reasonably assigned to silyl radical by quenching experiments using methylene chloride as a radical quencher. The wavelength dependence of the intermediate during photodegradation was observed for poly(phenylmethylsilane). The transient absorption spectrum obtained by the excitation at longer wavelength (σ,σ^* band region) showed a broad transient absorption near 400 nm. This was assigned to silyl radical by quenching experiments using methylene chloride as a quencher. When poly(phenylmethylsilane) was excited at shorter wavelength (π,π^* band region), an additional transient absorption appeared near 480 nm, which was assigned to be silylene using triethylsilane as a silylene trapping agent.

Introduction

Polysilanes have an intense absorption in the UV to near-UV region owing to the σ-delocalization along the linear Si–Si polymer backbone. Polysilanes are attracting considerable attention as mid- and deep-UV photoresists because of their high sensitivity for photodegradation.[1-3] Three possible reactions for the photodegradation of polysilanes have been proposed by Trefonas, West, and Miller on the basis of photodegradation product analysis:[4] first, the simultaneous extrusion of a silylene fragment and the formation of two silyl radicals, second, Si–Si bond homolysis and the formation of two silyl radicals, and third, the extrusion of a silylene fragment with simultaneous formation of a silicon–silicon bond. In their study, Trefonas et al. pointed out that the photochemical behavior of phenyl-substituted polysilanes is considerably more complex than that of alkyl-substituted polysilanes. Recently, the wavelength dependence of the photochemistry of polysilanes has been reported by Taylor et al.[5] Michl, Miller, et al. have also reported the wavelength dependence of photodegradation products of poly(dialkylsilanes);[6,7] the formation of dialkylsilylenes only occurs at relatively short excitation wavelengths below 300 nm. In the present paper we study the photolysis of two kinds of polysilanes, poly(cyclohexylmethylsilane) and poly(phenylmethylsilane). The excitation wavelength dependence of the photodegradation of polysilanes was investigated by time-resolved absorption spectroscopy, and the transient intermediates were assigned by quenching experiments.

Experimental Section

Materials. Polysilanes were prepared by Kipping reaction of diorganodichlorosilanes with sodium metal in toluene at 110 °C under rapid stirring. Polysilanes with a bimodal molecular weight distribution were fractionated by reprecipitation using 2-propanol–toluene mixed solvents, and then the molecular weight distributions were measured by gel permeation chromatography using monodisperse polystyrenes as standards: $M_w = 7220$, $M_w/M_n = 1.30$ for poly(cyclohexylmethylsilane), $M_w = 30.6 \times 10^4$, $M_w/M_n = 1.51$ for poly(phenylmethylsilane)-1, and $M_w = 3170$, $M_w/M_n = 1.16$ for poly(phenylmethylsilane)-2. Tetrahydrofuran (THF) which was dehydrated by sodium and degassed up to 10^{-5} Torr was used as a solvent for flash photolysis to avoid the quenching of silylene by moisture. Cyclohexane (Dotite Spectrozole) was dehydrated by calcium hydride and degassed up to 10^{-5} Torr. These solvents were transferred to a cylindrical quartz cell (10 cm long and 1 cm diameter) in a vacuum line.

Measurements. Xenon flash photolysis experiments were carried out using a 100-J lamp with a half-duration of about 10 μs. The decay curves of the transient absorptions were measured with a digital storage scope. The time-resolved absorption spectra were measured by a double-flash system using a stroboflash (half-duration of about 3 μs) as a monitor light and multichannel photodetector (MCPD). During the photolysis of poly(phenylmethylsilane)-1 and poly(phenylmethylsilane)-2, a band-pass filter (UV-D33S (240–410 nm)) and long-pass filter (UV-33 (300 nm–)) were used to select the excitation wavelength. All experiments were carried out at 22 °C.

Results

Time-Resolved Absorption Spectra of Polysilanes. The absorption spectra of poly(cyclohexylmethylsilane) and poly(phenylmethylsilane) are shown in Figure 1. The alkyl-substituted polysilane shows a σ,σ^* absorption band in the UV region. The phenyl-substituted polysilane shows a π,π^* absorption band in the UV region in addition to the σ,σ^* absorption band in the near-UV region. In the flash photolysis measurements, two kinds of optical filters were used to excite those absorption bands selectively. Figure 2 depicts the transmittance of the filters, UV-D33S and UV-33. When both filters are used, the σ,σ^* absorption band can be excited mainly. When only the UV-D33S filter is used, the σ,σ^* and the π,π^* absorption bands of poly(phenylmethylsilane) are excited.

Figure 3 shows the time-resolved absorption spectra for poly(cyclohexylmethylsilane) using only the UV-D33S filter. A similar spectrum was obtained when both UV-D33S and UV-33 filters were used. A sharp absorption peak appears at 370 nm with a weak absorption shoulder at about 430 nm. After the flash photolysis, these bands decrease uniformly as shown in Figure 3. The time-resolved spectra of poly(phenylmethylsilane) exhibited a quite different photochemical behavior from that of the alkyl-substituted polysilane. Figures 4 and 5 show the time-resolved absorption spectra for poly(phenylmethylsilane)-1 obtained using both UV-D33S and UV-33 filters and using only the UV-D33S filter, respectively. A broad absorption band appears near 400 nm in both figures. A noticeable spectral difference between σ,σ^* excitation and π,π^* excitation appears at about 480 nm. The transient absorption spectrum at 300 μs after the flash obtained

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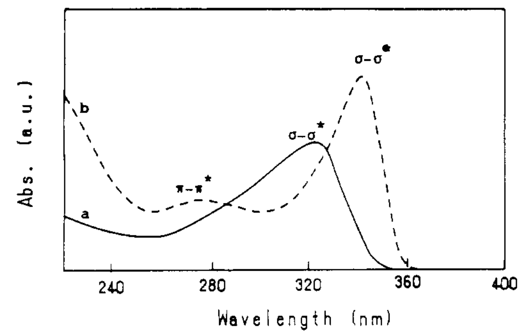

Figure 1. Absorption spectra of poly(cyclohexylmethylsilane) (a) and poly(phenylmethylsilane)-1 (b) in THF.

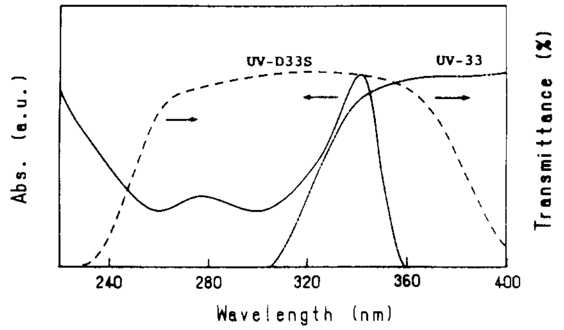

Figure 2. Transmittance of the filters and the absorption spectrum of poly(phenylmethylsilane)-1.

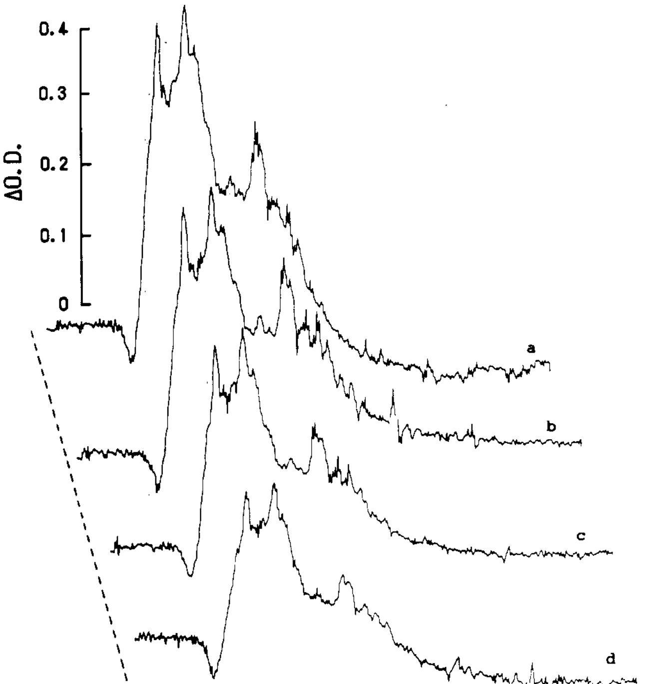

Figure 3. Time-resolved absorption spectra for poly(cyclohexylmethylsilane) excited using the UV-D33S filter in THF. Concentration: 1×10^{-3} M. Delay time after the flash photolysis: (a) 100, (b) 200, (c) 500, (d) 1000 μs.

using the UV-D33S filter is compared with that obtained using the UV-D33S and UV-33 filters in Figure 6. The spectral difference at about 480 nm is shown clearly. By π,π^* excitation, the absorption at about 480 nm increases. A similar wavelength dependence was observed for poly(phenylmethylsilane)-2 with lower molecular weight.

Quenching Experiments. The quenching experiments were effective in the assignment of the transient intermediates. The assignments of the transient absorption spectra obtained by flash photolysis were examined by using methylene chloride and triethylsilane as quenchers. It is known that silyl radicals readily abstract chlorine from chlorinated alkanes, and triethylsilane serves as an effective trap for silylenes.[4]

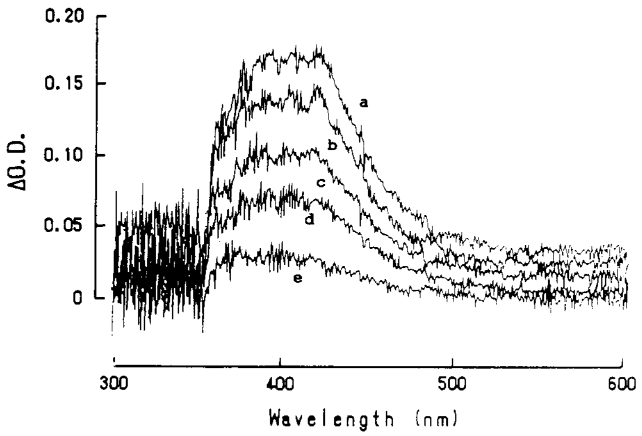

Figure 4. Time-resolved absorption spectra for poly(phenylmethylsilane)-1 excited using both UV-D33S and UV-33 filters in THF. Concentration: 1×10^{-3} M. Delay time after the flash photolysis: (a) 100, (b) 200, (c) 500, (d) 1000, (e) 3000 μs.

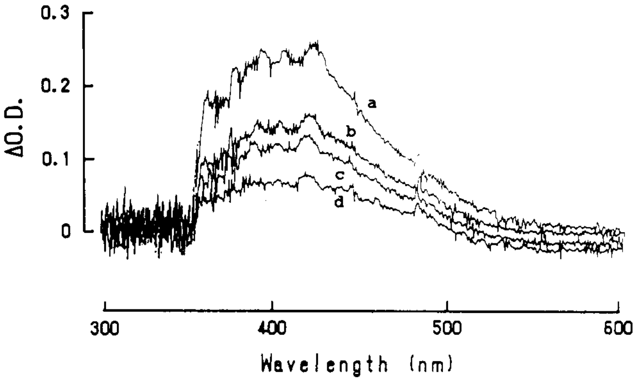

Figure 5. Time-resolved absorption spectra for poly(phenylmethylsilane)-1 excited using the UV-D33S filter in THF. Concentration: 1×10^{-3} M. Delay time after the flash photolysis: (a) 100, (b) 200, (c) 300, (d) 1000 μs.

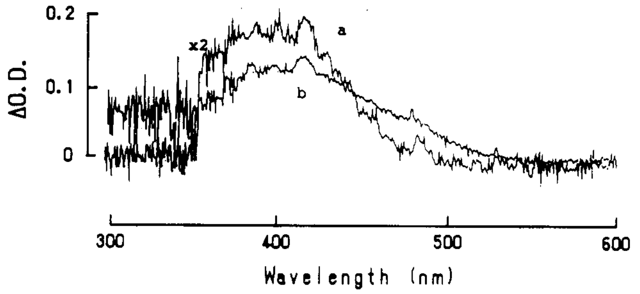

Figure 6. Dependence of the time-resolved absorption spectrum of poly(phenylmethylsilane)-1 on the excitation wavelength in THF: (a) UV-D33S and UV-33 filters, 300 μs after the flash photolysis; (b) UV-D33S filter, 300 μs after the flash photolysis. Concentration: 1×10^{-3} M.

The decay curves of the transient absorption of poly(cyclohexylmethylsilane) and the effect of the quencher are shown in Figure 7. The transient absorption at 370 nm is effectively decreased by the addition of a radical quencher, methylene chloride. Figure 8 shows first-order plots for the decay of the transient absorption of poly(cyclohexylmethylsilane) at 370 nm in the presence of methylene chloride. In the absence of the quencher, the decay of the transient absorption spectra did not obey simple first- or second-order kinetics. Even in the presence of the quencher at high concentration, the systems did not

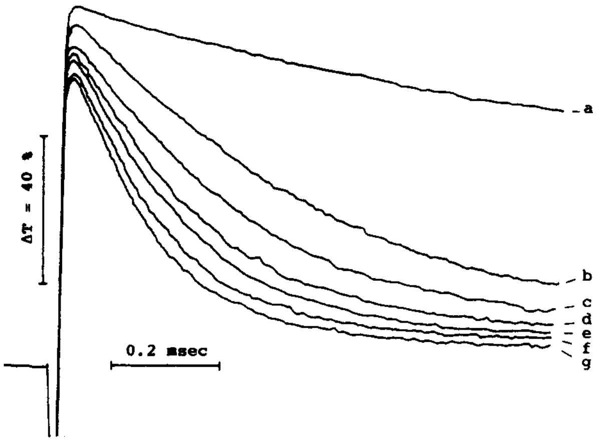

Figure 7. Effect of quencher (CH_2Cl_2) on the decay of the transient intermediates of poly(cyclohexylmethylsilane) at 370 nm excited using the UV-D33S filter in THF. Quencher CH_2Cl_2 concentration × 10^3: (a) 0, (b) 1.75, (c) 2.63, (d) 3.50, (e) 4.38, (f) 5.25, (g) 6.13 M.

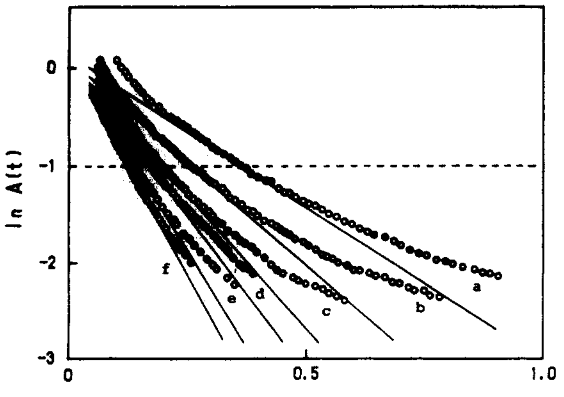

Figure 8. First-order plots for the decay of the transient absorption at 370 nm for poly(cyclohexylmethylsilane) excited using the UV-D33S filter in THF. Quencher CH_2Cl_2 concentration × 10^3: (a) 1.75, (b) 2.63, (c) 3.50, (d) 4.38, (e) 5.25, (f) 6.13 M.

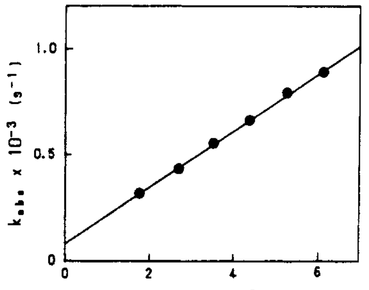

Figure 9. Plots of k_{obs} against the quencher CH_2Cl_2 concentration for the transient absorption of poly(cyclohexylmethylsilane) at 370 nm in THF. Filter used in the excitation: UV-D33S.

Table I
Quenching Rate Constants (k_q) for Polysilanes in THF

	k_q(Et_3SiH), M^{-1} s^{-1}	k_q(CH_2Cl_2), M^{-1} s^{-1}
poly(cyclohexylmethylsilane)/ 370 nm[a]	~0	1.34 × 10^6
poly(cyclohexylmethylsialne)/ 430 nm[a]	~0	1.27 × 10^6
poly(phenylmethylsilane)/ 370 nm[b]	~0	7.74 × 10^4
poly(phenylmethylsilane)/ 430 nm[b]	~0	8.53 × 10^4
poly(phenylmethylsilane)/ 500 nm[a]	4.11 × 10^5	8.21 × 10^4

[a] Filter: UV-D33S. [b] Filters: UV-D33S and UV-33.

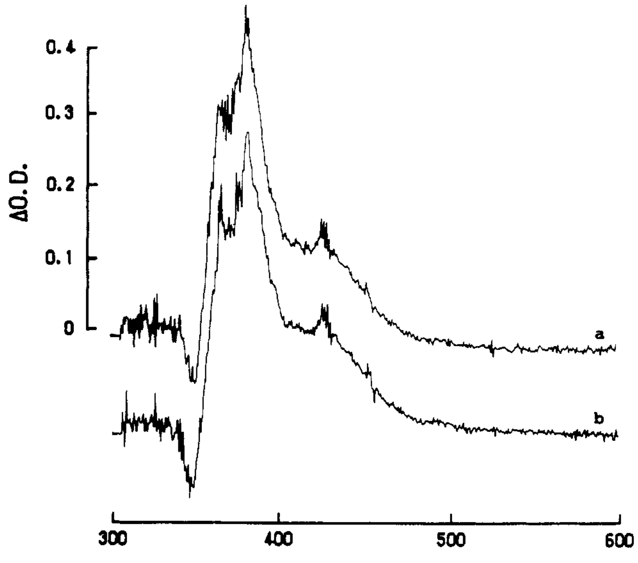

Figure 10. Time-resolved absorption spectra for poly(cyclohexylmethylsilane) excited using the UV-D33S filter in cyclohexane: (a) absorption spectrum in the absence of triethylsilane at 50 μs after flash photolysis; (b) absorption spectrum in the presence of 2 × 10^{-3} M triethylsilane at 50 μs after flash photolysis. Concentration: 1 × 10^{-3} M.

follow pseudo-first-order plots. This may be due to the high local concentration of transient intermediates in the polymer domain. The quenching constant of such mixed-order kinetics containing first and second order can be determined by monitoring the apparent rate constants k_{obs}, which are obtained from the tangential lines at the appropriate absorbance in the first-order plots as a function of quencher concentration.[8] The slope in the plots of k_{obs} against quencher concentration yields the quenching constant, k_q. Figure 9 shows the plots for the transient absorption of poly(cyclohexylmethylsilane) using methylene chloride as a quencher. From the slope, the quenching constant was determined as 1.34 × 10^6 M^{-1} s^{-1}. The quenching experiments for the transient absorption shoulder of poly(cyclohexylmethylsilane) at 430 nm gave a similar rate constant of 1.27 × 10^6 M^{-1} s^{-1}. On the other hand, the transient absorptions of poly(cyclohexylmethylsilane) at 370 and 430 nm were scarcely decreased by the addition of a silylene trap, triethylsilane.

The obtained quenching rate constants for poly(cyclohexylmethylsilane) and poly(phenylmethylsilane) are summarized in Table I. The quenching experiments for poly(phenylmethylsilane) show clearly the excitation wavelength dependence. We monitored the decay of the transient absorptions at three wavelengths: 370 and 430 nm by σ,σ^* excitation and 500 nm by π,π^* excitation. The transient absorptions at 370 and 430 nm by σ,σ^* excitation were effectively quenched by the radical quencher CH_2Cl_2 but scarcely quenched by the silylene trap Et_3SiH. On the other hand, the transient absorption at 500 nm by π,π^* excitation was effectively quenched by Et_3SiH.

Solvent Effect. The solvent effect on the photodegradation of polysilanes was investigated using the nonpolar solvent cyclohexane compared with the polar solvent THF. Figures 10 and 11 show the time-resolved absorption spectra of poly(cyclohexylmethylsilane) and poly(phenylmethylsilane)-2 in cyclohexane, respectively. The time-resolved absorption spectrum of poly(cyclohexylmethylsilane) in cyclohexane is similar to that in THF. In Figure 10, the time-resolved absorption spectrum in the presence of triethylsilane is also shown. There is no difference

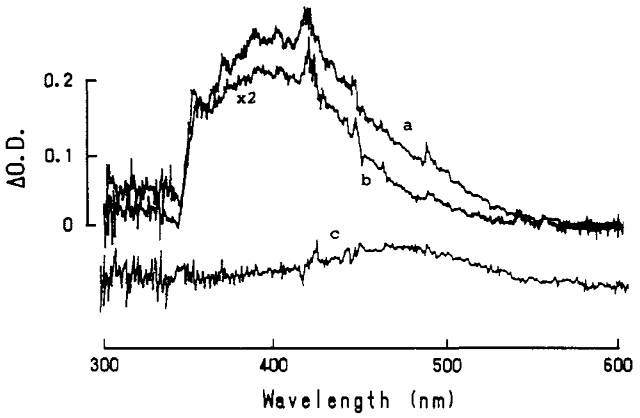

Figure 11. Dependence of the time-resolved absorption spectra of poly(phenylmethylsilane)-2 on the excitation wavelength in cyclohexane: (a) UV-D33S filter, 50 μs after the flash photolysis; (b) UV-D33S and UV-33 filters, 50 μs after the flash photolysis; (c) difference absorption spectrum which was calculated from spectrum a and spectrum b normalized at 400 nm. Concentration: 1×10^{-3} M.

between them in the absence and in the presence of triethylsilane. This same result was obtained in the quenching experiments. Low molecular weight poly(phenylmethylsilane)-2 was used because of its solubility in cyclohexane. In Figure 11, the transient absorption at about 480 nm by π,π^* excitation also appears in cyclohexane, but the absorbance decreases compared with that in the polar solvent THF. Spectrum c shows the difference spectrum which was calculated from spectrum a and spectrum b normalized at 400 nm. The transient absorption at 480 nm is shown clearly. In our experiments, the transient absorption near 480 nm could not be observed without dehydration of solvents and distillation into a cell on a vacuum line. The influence of the quenching of silylene by moisture in the solvent is significant.

Discussion

The spectral characterization of low molecular weight alkyl- and aryl-substituted silyl radicals was carried out by Chatgilialoglu et al. by laser flash photolysis.[9] They prepared a wide variety of silyl radicals by the proton abstraction reaction of *tert*-butoxy radicals from triorganosilanes. All of the silyl radicals they used show a very strong band near 300 nm and a weaker band/shoulder at longer wavelength. Triphenylsilyl radical shows a sharp absorption maximum at 328 nm and a broad absorption maximum at 420 nm. These spectra are similar to the spectrum obtained by the flash photolysis of poly(cyclohexylmethylsilane) in Figure 3. The absorption maximum of the poly(cyclohexylmethylsilyl) radical is somewhat red shifted compared to the low molecular weight silyl radicals reported by Chatgilialoglu et al.[9] This shift may be due to the σ-delocalization along the Si–Si polymer backbone. The assignment as a silyl radical was confirmed by quenching experiments using CH_2Cl_2 as a radical quencher and Et_3SiH as a silylene trap. The sharp absorption maximum at 370 nm was not quenched by Et_3SiH but effectively quenched by CH_2Cl_2 as shown in Table I. There is a possibility to assign the broad absorption band near 430 nm to a silylene. However, this possibility can be ruled out because the silylene trap Et_3SiH did not quench the absorption. The time-resolved absorption spectra in the absence and in the presence of triethylsilane also reject the possibility of silylene as shown in Figure 10. Furthermore, the good agreement between the k_q (CH_2Cl_2) at 370 and 430 nm supports the assignment as a silyl radical.

The photodegradation of cyclic and linear permethylpolysilanes was studied by Ishikawa, Kumada, et al.;[10] during the photolysis of cyclic compounds, silylene is the main intermediate. During the photolysis of linear compounds, silylene and silyl radical are produced as intermediates. The wavelength dependence of the photodegradation products of poly(dialkylsilanes) was reported by Michl, Miller, et al.[6,7] Trapping experiments using triethylsilane suggest the formation of dialkylsilylenes by short-wavelength excitation below 300 nm. Todesco and Kamat reported that silyl radical is the main intermediate during the laser flash photolysis of poly(dimethylsilylene-*co*-methyl(1-naphthyl)silylene).[11] Their excitation wavelength was the 337.1-nm line of a nitrogen laser. In our study, however, silylene was not observed during the photolysis of an alkyl-substituted polysilane, poly(cyclohexylmethylsilane), even by short-wavelength excitation below 300 nm. It is probable that the lifetime of cyclohexylmethylsilylene is too short to detect by our flash photolysis system. Levin et al. have reported that the half-life of dimethylsilylene gas is about 1 μs.[12] Recently, picosecond laser photolysis of poly(phenylmethylsilane) was reported by Ohsako et al.[13] They observed the formation of silylene in spite of longer wavelength excitation at 355 nm. Such a discrepancy may be induced by the difference of photon density between steady-state irradiation and laser pulse irradiation. Michl et al. have mentioned that the energy of the photon at 254 nm (112.5 kcal/mol) and the energy of the relaxed lowest excited singlet state (85–90 kcal/mol) are too small for a simultaneous rupture of two Si–Si bonds upon absorption of a single photon.[6] The simultaneous extrusion of a silylene fragment and the formation of two silyl radicals by the single-photon energy is indeed energetically improbable. On the other hand, the formation of silylene by a one-photon process may be possible through a concerted process. The extrusion of silylene formation with the simultaneous formation of a silicon–silicon bond may be energetically feasible. The net effect is the breakage of one silicon–silicon bond by one photon. The mechanism of the formation of silylene is a complicated problem. Two factors, the photon energy and the density, are important in the formation of silylene.

Ohsako et al. depicted the transient absorption spectrum for poly(phenylmethylsilane).[13] At 300 ps after the laser flash photolysis, only the 450-nm peak was observed. A sharp absorption band at 370 nm and a broad absorption band at 450 nm were observed at 50 ns, and the transient absorption spectrum gradually changed into a broad absorption band near 400 nm with increasing delay time. The assignment of the 450-nm band to silylene was suggested. However, Ohsako et al. mentioned that the possible contribution of silyl radicals to the transient absorption spectra should not be dismissed; the origin of the 370-nm band is unknown, though the possibility exists that it corresponds to a chain-based radical which was formed by scission in the middle of a chain. Comparison of the transient absorption spectra in our study with Ohsako et al.'s results is possible only in the long delay time region after 50 μs. In the long delay time region, our spectra for poly(phenylmethylsilane) are consistent with their spectra. The quenching experiments suggest that the transient absorptions at 370 nm are not assigned to silylene but to silyl radical. These absorptions are reasonably assigned to silyl radical which may be formed in the middle of the polymer chain because the magnitude of the quenching rate constants (10^4 M^{-1} s^{-1}) is smaller than that for low molecular weight radicals.[14]

West et al. have reported that methylphenylsilylene shows the absorption maximum at 490 nm in a glassy solution at 77 K.[15,16] Gaspar et al. have reported the absorption maximum of methylphenylsilylene to be 440 nm in cyclohexane using laser photolysis.[17,18] The half-life was determined to be 75 μs.[18] Ohsako et al. reported the absorption maximum of methylphenylsilylene to be 450 nm in THF.[13] However, the absorption decayed within 1 μs. The formation of silylene–ether complexes in a glassy solution has been reported by West et al.[19] Upon annealing of the matrix, the absorption of silylene at longer wavelength disappeared and a new absorption at about 350 nm appeared, which was assigned to a silylene–ether complex. Ohsako et al.[13] suggested the possibility of silylene–solvent (THF) complex formation during the photodegradation of poly(phenylmethylsilane) to explain the similarity between the transient absorption spectrum in THF and that in THF/MeOH (10%) because MeOH is known to be an effective silylene trap as reported by Gaspar et al.[17,18] In our case, a long-lived transient intermediate was observed at 480 nm not only in cyclohexane but also in THF by xenon flash photolysis. The absorption maximum shifts to longer wavelength compared to those determined by laser flash photolysis. In the case of laser flash photolysis, a low molecular weight silylene must be produced effectively due to the high photon density. The absorption of silylene measured by xenon flash photolysis corresponds to the absorption tail of the decay curve of silylene, in which only the long-lived component can be detected. The shift of the absorption maximum to longer wavelength in our case may be explained by considering a stabilized silylene, for example, a silylene attached to the polymer chain. It is likely that the silylene detected under our experimental conditions is a dissociated one from a silylene–ether complex. Recently, McKinley et al. have reported the formation of disilylsilylene by UV irradiation of poly(di-*n*-alkylsilane)s, which are produced by reductive elimination.[20] The presumed intermediate in our reaction would be such a stabilized chain silylsilylene.

The flash photolysis of poly(phenylmethylsilane) exhibited a significant excitation wavelength dependence. When poly(phenylmethylsilane) is excited at longer wavelength (σ,σ^* band), silyl radicals are produced. Silylene and silyl radicals are produced by shorter wavelength (π,π^* band) excitation. One explanation is that such a wavelength dependence is due to a high photon energy at shorter wavelength as reported on poly(dialkylsilane).[6,7] Another explanation may be possible for aryl-substituted polysilanes considering the intramolecular charge-transfer excited state between the aromatic group and the disilyl group. Horn and Whitenack have reported that (phenylethyl)pentamethyldisilanes with various substituents exhibit intramolecular charge-transfer spectra at 77 K which should involve σ(SiSi)–π^* charge-transfer states.[21] Sakurai et al. have also reported the formation of a $^1(\sigma\pi^*)$ orthogonal intramolecular charge-transfer state on the basis of the fluorescence spectra of aromatic disilyl compounds with various substituents.[22] In the $^1(\sigma\pi^*)$ orthogonal intermolecular charge-transfer state, the disilyl group is a donor and the excited aromatic group is an acceptor. Ito, Azumi, et al. have reported that the broad emission of poly(phenylmethylsilane) at longer wavelength is more enhanced when the excitation is carried out at π,π^* absorption bands of the phenyl substituent as compared to the excitation at σ,σ^* absorption bands of the silicon skeleton and concluded that the broad emission bands are not an emission from the (π,σ^*) state but an emission from the intrapolymer skeleton σ to the pendant π^* charge-transfer state.[23] The emission from the ($\sigma\pi^*$) state can be observed only at quite low temperature. The ($\sigma\pi^*$) state may be unstable at room temperature, and silylene may be produced by the dissociation or secondary photolysis of the ($\sigma\pi^*$) state.

Energy migration should play an important role in the photodegradation of polysilanes. Recently, Hochstrasser, Zeigler, et al. have reported the excited-state dynamics of polysilanes.[24-26] They suggested that the picosecond energy transfer in polysilanes effectively deposits almost excitation energy in the longest all-trans segments, and other photophysical and photochemical events occur from these longest and lowest segments. It has been estimated from femtosecond time-resolved excited-state absorption spectroscopy that 25 silicon atoms are the upper limit for the average excitation state conjugation length of poly(di-*n*-hexylsilane).[26] The photodegradation of polysilane properly occurs after the energy migration. In our study two kinds of poly(phenylmethylsilane)s, a higher molecular weight one and a lower molecular weight one, were used. The degree of polymerization of the former is about 2000 and that of the latter is about 25. In the case of the transient absorption spectrum of silyl radical, the molecular weight dependence did not appear in our experiments as shown in Figure 4 for the higher molecular weight one and Figure 11 for the lower molecular weight one.

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Registry No. $MeSiCl_2$-cyclo-C_6H_{11} (homopolymer), 88002-85-1; (MeSi-cyclo-$C_6H_{11})_n$ (SRU), 88003-16-1; $MeSiCl_2Ph$ (homopolymer), 31324-77-3; $(MeSiPh)_n$ (SRU), 76188-55-1.