Dynamics of Silylenes in Polysilylenes with Structural Defects by Excimer Laser Flash Photolysis

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The dynamics of silylene extrusion reaction was observed in polysilylene with Si branchings by using KrF excimer laser flash photolysis technique. The initial yield of silyl radicals was seen to be dependent on the backbone structure of polysilylenes, whereas the yield of silylenes was almost proportional to the number of the linear Si units in their backbones.

Polysilylenes have elicited great interests because of their interesting optical and electronic properties, high sensitivity to UV light or other radiations.[1] The photodegradation of polysilylenes in the solid phase or in solution is of considerable interest, and has been shown to produce silylenes, polysilylated silyl radicals, and ionic species as reactive intermediates upon exposure to UV light and radiation sources.[2–6] Silyl radicals are expected to play a crucial role not only in the photochemical reactions in polysilylenes, but also in silicon chemistry as sensitive photoinitiators for polymerizations or as precursors to promote π-system such as Si=Si and Si=C species.[7,8] Possible reactions have been suggested to result in the silylene extrusion from a Si backbone of organopolysilylenes, implying the dependence of the yield on the backbone conformation. In the present letter, transient spectroscopy of the reactive intermediates is carried out for polysilylenes with Si branchings using KrF excimer laser flash photolysis technique, and the dynamics of silylene extrusion reactions is discussed in relation with that of polysilylated silyl radicals.

Poly(methlyphenylsilylene) (PMPS)[9] and PMPS with Si branchings: PSi(D = x)[9] were prepared by Wurtz coupling of the various proportional mixture of methylphenyldichlorosilane and *p*-tolyltrichlorosilane (purchased from Shin-Etsu Chemical Co. Ltd.) using sodium metal. D is the ratio of ^{1}H NMR signal intensities due to *p*-tolyl methyl and Si-methyl groups, and this indicates the degree of branching of the polysilylene chain. The IR spectra of the polymers suggested no considerable increase in the number of Si–O bondings with increasing D. The polymer was dissolved in cyclohexane (Dojin Chemicals) at 2 mM concn (Base Mol Unit), and the solutions were Ar bubbled prior to use. Excimer laser was driven with KrF gas at 248 nm, and the laser pulses were attenuated down to 20 mJ/(cm^2·pulse). Exposure was performed with the pulse with fwhm 5.4–8.2 ns. The details in the set of apparatus are already described elsewhere.[10–12]

Figure 1 shows transient absorption spectra of the polysilylene solutions in cyclohexane. All absorption spectra suggest the overlap of two transient absorptions at ~350 nm (A band, taking the effects of bleaching of steady state absorption into accounts) and ~480 nm (B band). The A and B bands are ascribed to the absorptions of polysilylated silyl radicals and silylenes, respectively, because of their quenching by CCl_4 and 1,4-hexadiene as shown together with the transient spectra in Figure 1.[13,14] The kinetic traces at 380 nm give the rate con-

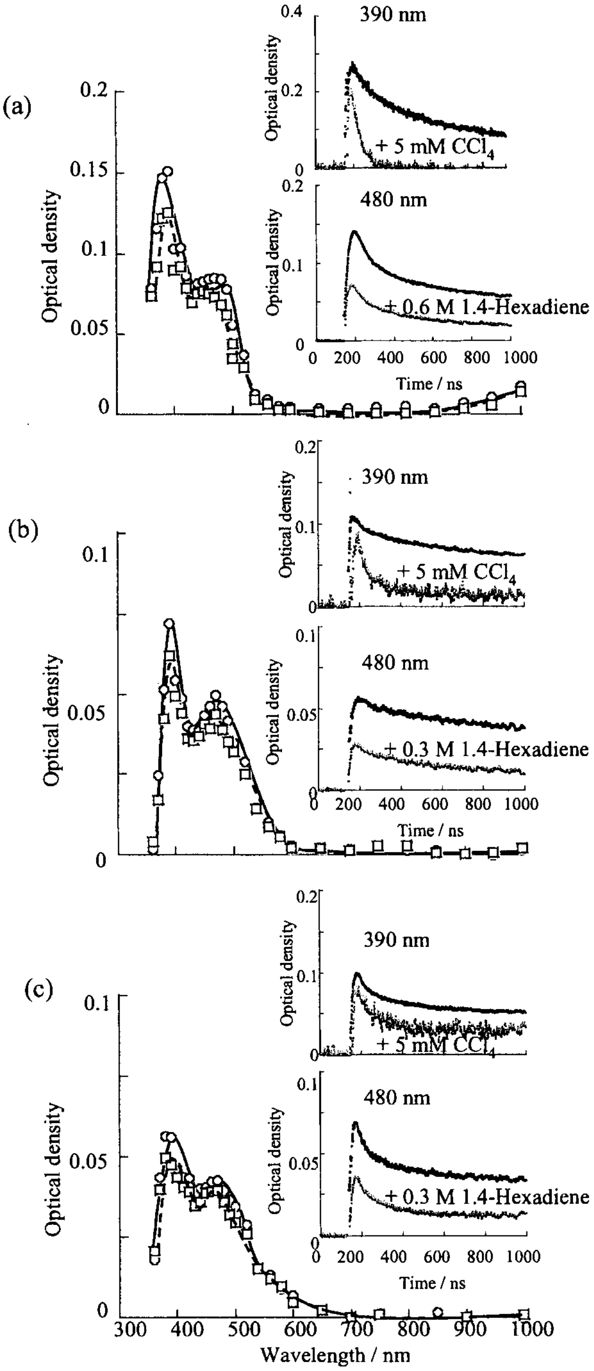

Figure 1. Transient absorption spectra, of (a)PMPS(D = 0), (b)PS (D = 0.15), and (c) PS(D = 0.32) in 1 mM cyclohexane solution. Solid and dashed lines denote the spectra recorded at 200 (circles-solid) and 500 ns (squares-dashed) after pulses, respectively. Superimposed figures show kinetic traces of the chromophore ascribed to silyl radicals and silylenes.

stants of silyl radical extinction as $k_A = (1.1–4.6) \times 10^5$ s^{-1}. The kinetic traces of A band are also recorded under a variety of CCl_4 concentrations, and the scavenging rate constants: k_{sc} are determined as 1.0×10^9, 8.3×10^8, and 4.9×10^8 M^{-1}s^{-1} for PMPS, PSi(D = 0.15), and PSi(D = 0.32), respectively. It is considerable that the two types of silyl radicals (–RR'Si$^\bullet$ and –RSi$^\bullet$–) are formed simultaneously in the photolysis of these polymers. Based on the values of k_{sc}, the initial yields of silyl radicals are determined for the polymers, and they depend strongly on the values of D as displayed in Figure 2.

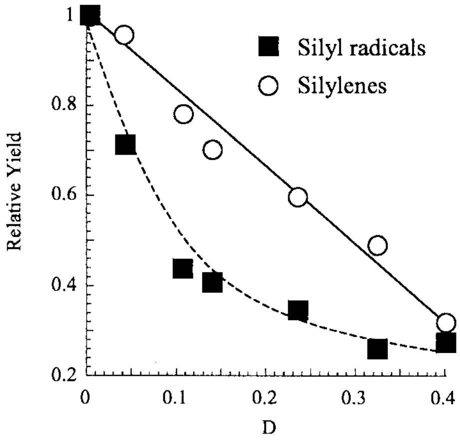

Figure 2. Dependence of the yield of silyl radicals (squares-dashed) and silylenes (circles-solid) on D. The values are relative to the yield in PMPS.

The kinetic trace of the B band for all the polymers becomes analogous to that of A band by adding hexadiene at the sufficient concentration for silylene trapping, suggesting the overlapping of the tail of the A band. The decay of B band consists of two components (B_f and B_s), and the decay rate of the fast component: B_f is consistent with k_A of A band, supporting the overlap of A band at 480 nm. The transient spectrum indicates the higher yield of B band in linear PMPS than that in PSi(D = x)s by taking account of the contribution of the A band. The relative yields of silylenes are calculated for all the polymers on the basis of k_A as follows,

$$\Delta^{OD}(t) = \alpha \exp(-k_A t) + \beta$$

where Δ^{OD} is the observed optical density at B band, α is the constant, and β is the apparent initial yield of silylenes. The values of the yield vs D are plotted in Figure 2. The yields of silylenes gradually decrease with increasing D in the polymer backbone. The yield reaches to 0 at D = ~0.5 by the extrapolation of the linear relationship, suggesting that the silylene extrusion requires the linear Si catenation having 1–2 Si units. The yield of silyl radicals, however, decreases abruptly with an increase in D, and seems to be saturated at D > 0.5. This suggests that the efficiency of the Si–Si homolysis depends strongly on the length of the linear Si catenation, and the intramolecular energy transfer gives a good interpretation to the saturation in the yield at the higher D.

In summary, 248-nm UV exposure produces silylenes and silyl radicals at the linear Si catenation in PMPS and PMPS with Si branchings, and the silylenes and silyl radicals are observed independently within the time range. Silylenes can be produced even in a few membered linear Si catenation, whereas the length of the Si catenation affects the yield of silyl radicals.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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9 PMPS: ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 7.1(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –39.2, –39.8, –41.2, $M_w = 3.2 \times 10^4$, $M_w/M_n = 2.7$. PSi(D = 0.05): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.2(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.1, –39.8, 41.2, –45.8, $M_w = 2.0 \times 10^4$, $M_w/M_n = 3.5$. PSi(D = 0.11): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.2(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.2, –39.8, 41.2, –46, $M_w = 2.1 \times 10^4$, $M_w/M_n = 3.9$. PSi(D = 0.15): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.1(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.2, –39.8, –41.2, –46, $M_w = 1.9 \times 10^4$, $M_w/M_n = 3.7$. PSi(D = 0.23): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.2(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.2, –39.8, 41.2, –46, $M_w = 1.5 \times 10^4$, $M_w/M_n = 3.1$. PSi(D = 0.32): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.2(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.2, –39.8, –41.2, –46, $M_w = 1.1 \times 10^4$, $M_w/M_n = 2.6$. PSi(D = 0.40): ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.2(br), 2.3(br), 7.2(br); ^{29}Si NMR (119.19 MHz, $CDCl_3$) δ –35, –39.2, –39.9, –41.2, –45.9, $M_w = 1.3 \times 10^4$, $M_w/M_n = 4.1$.
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