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Communications to the Editor

Novel Polysilane Synthesis Using Photochemical Vapor Deposition

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Polysilane polymers have attracted much attention owing to their unique electronic properties based on the delocalized σ-electrons over the silicon backbone and their potential applications for new materials such as microelectronics and integrated optics.[1] Several synthetic methods for polysilanes have been reported that include the conventional Wurtz-type coupling of halosilanes,[1a] the anionic polymerization using masked disilenes,[2] the ring-opening polymerization of cyclic oligosilanes,[3] the catalytic dehydrogenative coupling of hydrosilanes,[4] and the electrochemical reduction of halosilanes.[5] Because all these syntheses are carried out in the liquid phase, it has been very difficult to prepare polysilane polymers with low solubility such as poly(dimethylsilylene) and poly(dipropylsilylene) by these methods.

The method for chemical vapor deposition (CVD) is highly promising as a synthetic process for less soluble and/or crystalline polysilanes. We wish herein to report a novel synthetic method for a linear polysilane using a photo-CVD method of a small cyclic oligosilane. No linear polysilane has been synthesized by CVD methods until now, even though the methods have been applied to obtain several silicon-based polymers. Poly(carbosilane)s were synthesized by Okutani et al. using a laser ablation of poly(methylphenylsilylene).[6] A network polysilane was obtained by Watanabe et al. using photolysis of methylphenyldichlorosilane in a gas phase.[7]

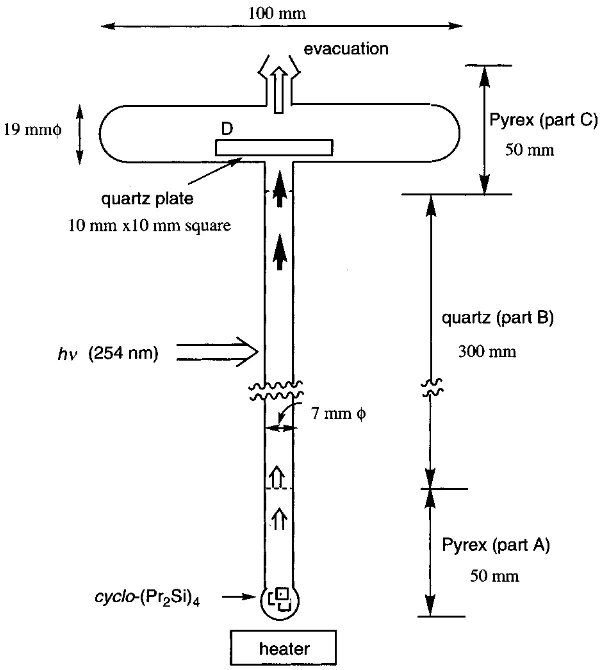

Figure 1. An apparatus for photo-CVD of poly(dipropylsilylene); ca. 1.0 × 10^{-2} Torr at 270 °C.

Our polymerization is based on the vapor-phase photolysis of a small ring oligosilane. Photolysis of octapropylcyclotetrasilane (**1**)[8,9] was carried out in an apparatus shown in Figure 1. Typically, cyclotetrasilane **1** (50 mg, 0.110 mmol) was placed in part A of the apparatus and then vaporized by heating the bottom of the apparatus up to ca. 270 °C under vacuum. The vapor of **1** (ca. 1.0 × 10^{-2} Torr) was irradiated with a spiral low-pressure mercury arc lamp (110 W) through quartz part B in Figure 1. During the photolysis, products deposited to form an amorphous film on a quartz square plate D (10 mm × 10 mm), which was placed at the top of the apparatus. The surface of quartz plate D used

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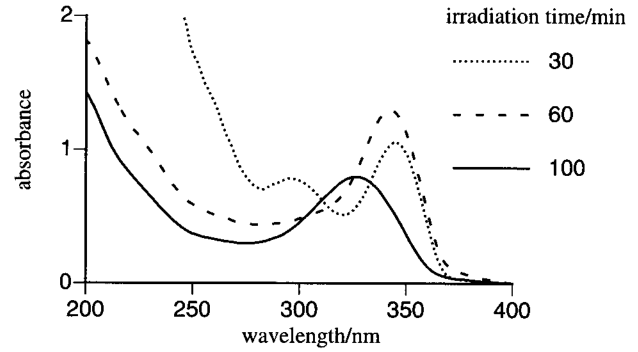

Figure 2. Absorption spectra of the poly(dipropylsilylene) films deposited on quartz plates depending on the irradiation times.

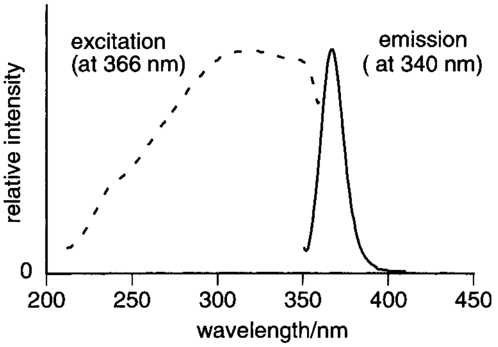

Figure 3. Emission and excitation spectra of a poly(dipropylsilylene) film obtained by the photo-CVD method.

here was pretreated with 10 wt % NaOH(aq) to cleave SiOSi linkage on the surface and then with dimethyldichlorosilane followed by the reduction using lithium aluminum hydride. All the starting material was consumed after 60 min irradiation. The resulting film showed an absorption maximum at 345 nm (Figure 2, dashed line). The thickness of the film was not determined but roughly estimated to be a few tens of nanometers on the basis of the optical density of the absorption maximum. The photoluminescence spectrum of the film showed an emission band at 366 nm with a small Stokes shift and a narrow bandwidth (Figure 3); no other emission bands were observed in the longer wavelength region. On the basis of the similarity of these spectral features as well as the excitation spectral pattern with those for reported poly(dialkylsilylene)s,[1a,10] the film was determined to consist of poly(dipropylsilylene)s without branching.

The UV absorption spectra of the polysilane films thus obtained depended significantly on the reaction conditions. At a constant bottom temperature, the spectra depended on the irradiation times. As shown in Figure 2, two absorption maxima were observed at 345 and 295 nm for the film obtained after 30 min irradiation. The former band is assigned to poly(dipropylsilylene), while the latter would be due to linear oligosilanes such as decasilanes; the absorption maximum is reported to be 294 nm for perpropyldecasilane at 293 K in 3-methylpentane.[11] As mentioned above, the film obtained after 60 min irradiation showed a typical spectral feature for linear polysilanes with no bands due to the oligosilanes. However, prolonged irradiation (100 min) caused significant decomposition of the polysilanes as evidenced by the blue shift of the absorption band maximum to ca. 330 nm. The polysilane on the quartz plate is suggested to decompose by the scattered light.

A plausible mechanism for the polymerization is shown in Figure 4. In this mechanism, a key reactive species of the polymerization is assumed to be dipropylsilylene, which is formed by the photolysis of cyclotetrasilane **1**.[12,13] Consecutive insertion of the silylene to the Si–H bonds on the surface of plate D will give the polysilane film.

Since disilene $Pr_2Si{=}SiPr_2$ and trisilane-1,3-diyl $^\bullet(Pr_2Si)_3{}^\bullet$ can also be generated during photolysis of **1**, these species may serve as key intermediates during the polymerization.[13,14] However, the following results and discussion eliminate these possibilities. Disilene $Pr_2Si{=}SiPr_2$ may react with (Si)O–H on the quartz surface to give $(Si)OSiPr_2SiPr_2{-}H$ groups. However, the disilene would not be involved in the propagation step because Si=Si double bonds are known not to react with Si–H bonds. If the trisilane-1,3-diyl assumes an important role in the polymerization, the terminal active site

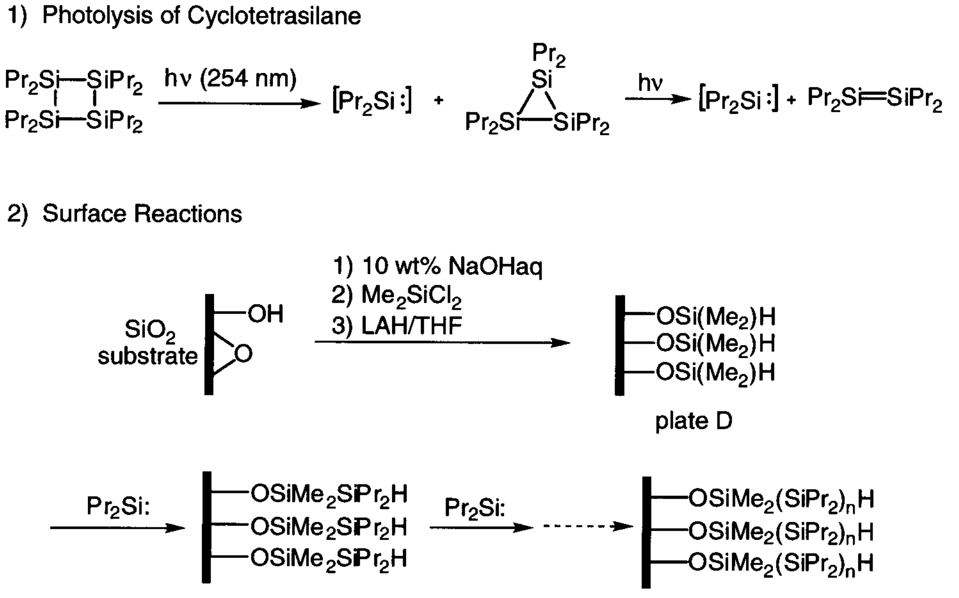

Figure 4. A plausible mechanism for the propagation of poly(dipropylsilylene) on a pretreated quartz surface (D) through photolysis of octapropylcyclotetrasilane (**1**).

during the polymerization should be silyl radicals. Since silyl radicals are known to be good initiators of the polymerization of styrene,[1a] polystyrene would be formed if the photolysis of **1** is performed in the presence of styrene. In reality, no polystyrene was observed on the quartz surface during such an experiment.

The above silylene mechanism was supported by several additional experiments. When a quartz plate was pretreated with triethylsilanol to cap Si−OH groups by trialkylsilyl groups on the surface (plate D′), no polysilane film was produced during the photo-CVD of cyclotetrasilane **1**, as evidenced by UV spectroscopy. On the other hand, when the surface of a quartz plate was cleaned by treating with concentrated H_2SO_4 (plate D″), a polysilane film was formed during the irradiation. However, the optical density for the 345 nm band of the film was 10 times lower than that of the film formed on plate D in the same conditions. It is suggested that, on the surface of plate D″, insertion of the silylene to (Si)O−H bonds should occur at the initial step of polymerization, but a significant amount of surface silicon atoms is deactivated by the Si−O−Si linkage.

The current new method is highly promising for preparation of films of various linear polysilanes.

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(8) Octapropylcyclotetrasilane (**1**) was prepared by the following procedure. To sodium dispersion (5.06 g, 220 mmol) in toluene (100 mL), dipropyldichlorosilane (18.5 g, 100 mmol) was added dropwise, and then the mixture was stirred at reflux for 8 h. Usual workup, Kügel-rohr distillation, and then recrystallization from ethanol afforded pure **1**: mp 66.5 °C; colorless crystals; yield 32%. ^{1}H NMR ($CDCl_3$): δ 0.93−1.09 (m, 40H), 1.42−1.62 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 14.6, 18.5, 20.9. ^{29}Si NMR ($CDCl_3$): δ −21.6. MS *m/z* (rel intensity): 456 (M+, 100), 414 (10), 372 (37), 330 (60), 288 (51), 246 (28), 214 (35), 161 (60), 144 (30). HRMS Found: 456.3422. Calcd for $C_{24}H_{56}Si_4$: M, 456.3455.

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(13) Irradiation with a low-pressure mercury arc lamp (110 W) of **1** in hexane in the presence of 2,3-dimethyl-1,3-butadiene as a trap afforded the corresponding 1,1-dipropyl-3,4-dimethyl-1-silacyclopentan-3-ene, 1,1,2,2-tetrapropyldisilane, and 1,1,2,2,3,3-hexapropyltrisilane as major products. The results are similar to the photolysis of other peralkylcyclooligosilanes.[12]

(14) A tetrasilane-1,4-diyl $^\bullet(Pr_2Si)_4{}^\bullet$ may be generated through the thermal ring opening of **1**, but the biradical would not participate in the present photochemical polymerization because no thermal decomposition of **1** occurred up to 320 °C. Thermal ring-opening polymerization using a cyclotetrasilane has been reported: Rulkens, R.; Resendes, R.; Verma, A.; Manners, I.; Murti, K.; Fossum, E.; Miller, P.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 8165.

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