Vacuum-Deposited Thin Film of Linear Oligosilane $Me(SiMe_2)_{12}Me$

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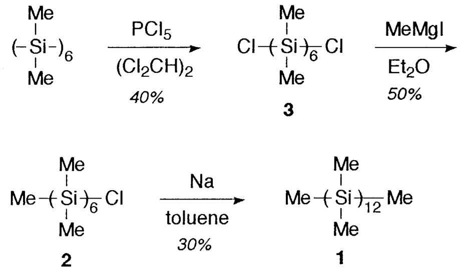
Thin film of linear oligosilane, $Me(SiMe_2)_{12}Me$, was prepared by a vacuum-deposition method. In the film, the Si-backbones adopted all-*trans* conformation and highly oriented perpendicular to the substrate. The oligosilane film showed a sharp UV absorption at 285 nm attributed to the planar-zigzag form.

Linear oligosilanes, $Me(SiMe_2)_nMe$, have recently attracted considerable attention as fundamental models for understanding the relationship between the conformations and the electronic properties, which are attributed to σ-electrons delocalized over silicon backbone chains, of polysilanes $(SiRR')_n$ with R = R' = alkyl.[1,2] The properties of oligosilanes have been measured in solution or in matrix, but there is no report on the properties in the solid state.[2b-f] This is partly because of the difficulty in preparation of solid samples (*e.g.* single crystals and oriented films), whose molecular structures can be determined by X-ray analysis. Recently, a vacuum-deposition method has been used as one of the powerful methods to form organic thin films, and oriented thin films of polydimethylsilane have been prepared by Furukawa *et al.*[3] and us.[4] The cleavage of the Si-Si bonds of the polymer, however, were unavoidable due to the high temperature up to 400 °C during the vacuum-deposition. The molecules in the films were thermally decomposed to a certain length of Si-catenations containing small amounts of Si-O-Si, $Si-CH_2-Si$, and Si-H bonds.[4] Oligosilanes, $Me(SiMe_2)_nMe$, have melting points without decomposition (*e.g.* 63 °C for n = 8, 153 °C for n = 12, and 198 °C for n = 16), in clear contrast to polydimethylsilane.[5] Thus, oligosilanes are expected to be vacuum-evaporated under a milder condition than that for the polymer, and there would be no cleavage of the Si-Si bonds. Herein, we report the preparation of vacuum-deposited thin film of $Me(SiMe_2)_{12}Me$ **1** together with the X-ray analysis and the UV absorption spectra of the film.

Permethyldodecasilane **1** was synthesized by a coupling reaction of 1-chloropermethylhexasilane **2**, which is available by two steps from dodecamethylcyclohexasilane, with sodium in toluene according to Scheme 1[6] and purified by sublimation and subsequently with a preparative HPLC.

Under vacuum of 5×10^{-6} Torr, powder of oligosilane **1** was heated in a quartz pot at 125-130 °C and deposited on a quartz plate at room temperature for *ca.* 20 min. A thickness monitor with a quartz oscillator was used to monitor the rate of the vacuum deposition and the amount of the deposited molecules. The thickness of the resulting film was estimated to be *ca.* 2000 Å by the monitor. There is no change in the chemical structure of the oligosilane **1** through the vacuum-deposition, since the IR spectrum of the deposited molecules is the same as that of powder before the deposition.



Scheme 1.

Figure 1 shows X-ray diffraction pattern of the vacuum-deposited film of oligosilane **1**, measured by a reflection method. A series of reflections with long spacing of 25.7 Å, assigned to 00*l*, was observed up to at least 8th order, and other reflections such as *hk*0 or *hkl* were not found. The spacing is quite

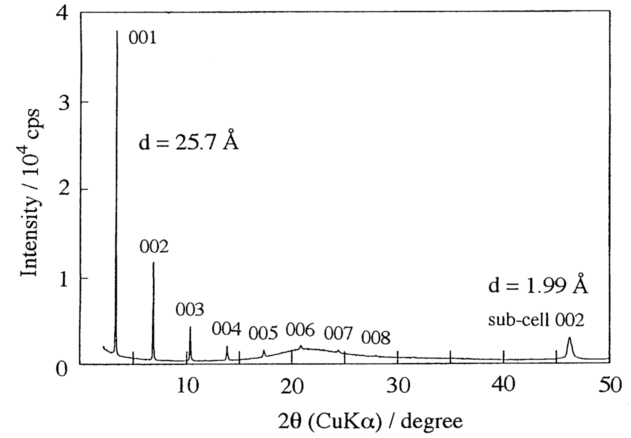


Figure 1. X-ray diffraction pattern of the vacuum-deposited thin film of oligosilane **1**.

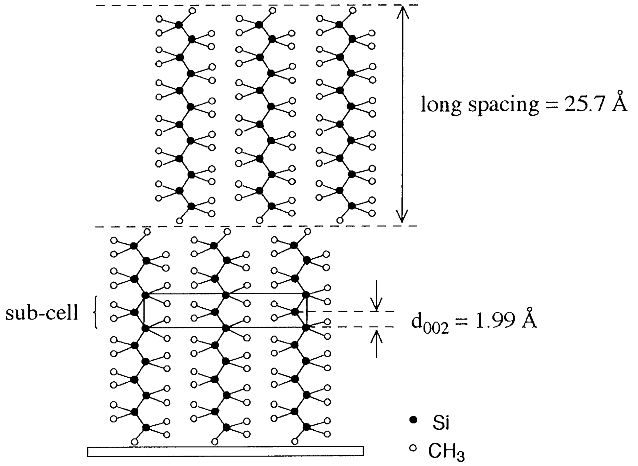


Figure 2. Schematic illustration of the multilayer structure of oligosilane **1** in the vacuum-deposited thin film.

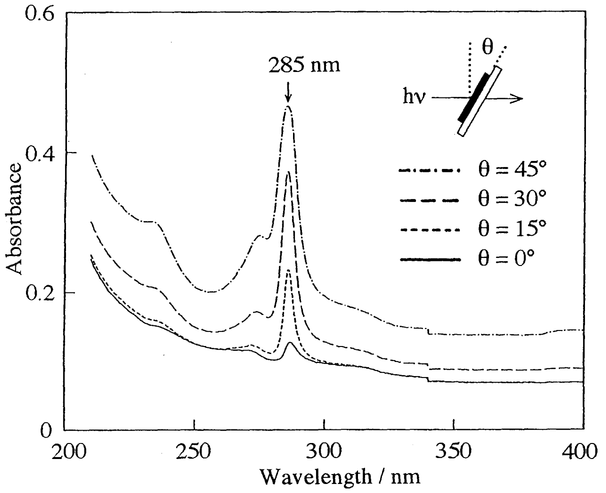


Figure 3. UV absorption spectra of the vacuum-deposited thin film with the tilted angle θ (0, 15, 30, and 45°) of oligosilane **1**.

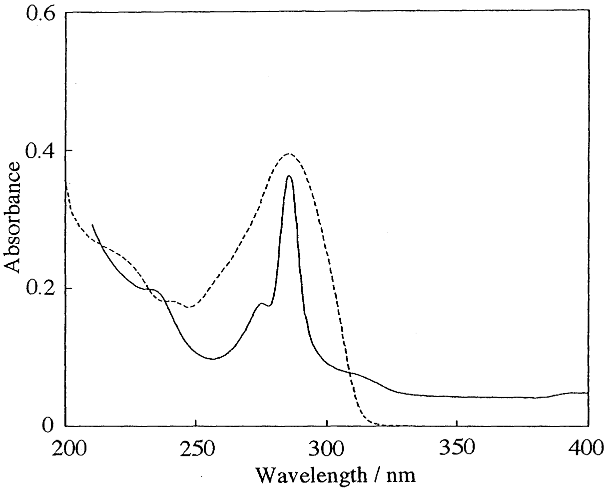


Figure 4. UV absorption spectra of oligosilane **1** in the vacuum-deposited film at a tilted angle 45° (——) and in a hexane solution (- - - -).

consistent with the extended molecular length of oligosilane **1** estimated from a molecular model. In addition, a strong reflection with d-spacing of 1.99 Å (2θ = 45.6°) corresponding to sub-cell 002 was observed. This spacing is very close to that in polydimethylsilane $(SiMe_2)_n$, 1.94 Å, which was found to adopt all-*trans* conformation in the solid state by electron diffraction method.[7] These results undoubtedly demonstrate that the Si-backbones with all-*trans* conformation of oligosilane **1** are highly oriented perpendicular to the substrate, and form a regular layer structure as schematically illustrated in Figure 2.

The UV absorption of the film of oligosilane **1** is of particular interest. Figure 3 shows the change of UV spectra of the film with the inclination angle of the film θ (0, 15, 30, and 45°). Very small absorption bands were observed when the UV beam was normal to the film (θ = 0°). When the film was tilted (θ = 15, 30, and 45°), a sharp absorption band with a maximum at 285 nm appeared. The intensity of the band increased remarkably as the inclination angle of the film became larger. This spectral change can be interpreted in terms of the perpendicular orientation of oligosilane **1** in the film. When the silicon main chains are perpendicular to the electric field, *i.e.* normal incidence of the UV beam, the absorption attributed to the σ-σ* transition cannot be observed, because of the delocalization of σ-electrons along the main chain. As the inclination angle increases, the main chain and the electric field form small angle and the intensity of the band increases. The same phenomenon was also found in the perpendicular-oriented film of polydimethylsilane prepared by us.[4] Figure 4 compares the UV absorption band of **1** in the film at a tilted angle 45° with that of **1** in a hexane solution. Whereas oligosilane **1** in the film exhibits a sharp band at 285 nm attributed to the all-*trans* conformer,[8] a broad shouldered band with a maximum at 285 nm is observed in solution, where some other Si-chain conformers coexist at equilibrium.

References and Notes

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8 A very small peak at 275 nm may be attributed to a nearly planar-zigzag form, not a decomposed compound.