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Low-Wavenumber Raman Scattering of Linear Oligosilanes

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Polysilanes, which contain only silicon atoms in the main chain with organic substituents, have attracted much interest because of their unique electronic and optical properties, such as electronic absorption, thermochromism, piezochromism, photoluminescence, conductivity, etc.[1−6] These properties are attributed to σ-electron delocalization along main chains.[7−9] Most of the modern interests, however, are focused on optical and electronic properties, and studies on the other basic properties are notably scant so far.[1] Poly(dimethylsilane) (PDMS), a simple representative of polysilanes, is an important polymer to understand basic properties of polysilanes. However, the insolubility of PDMS makes it difficult to process the polymer, *e.g.*, a film making, and its mechanical properties have not been measured. Elastic modulus is one of the important properties as a material, and estimation of the crystalline modulus is of interest. One method to estimate crystalline modulus is a calculation from all force constants of a polymer.[10] In the case of PDMS, only a few vibrational spectroscopic studies have been done,[11,12] and force constants of the polymer have not been determined yet. Another method is a calculation from frequency of longitudinal acoustic mode (LAM). LAM bands were first observed in Raman spectra of a series of *n*-alkanes, and their LAM frequencies were related to their elastic modulus and chain lengths.[13,14] Since then, LAM bands were observed among various polymers;[15−19] however, LAM bands of polysilanes have not been reported. In this study, Raman spectra of PDMS and its analogues, linear oligosilanes,[6] Me(SiMe$_2$)$_n$Me (n = 8, 10, and 12), were investigated in an attempt to find LAM bands. As LAM bands can be observed for chains of finite length and frequencies of LAM bands vary with molecular length, it is important to prepare well-defined oligosilanes with different lengths.

Permethyloctasilane (DM8), Me(SiMe$_2$)$_8$Me, was synthesized by a Wurtz coupling reaction of trimethylchlorosilane and 1,6-dichlorododecamethylhexasilane (DM6Cl) with sodium in toluene according to Scheme 1. Permethyldecasilane (DM10), Me(SiMe$_2$)$_{10}$Me, permethyldodecasilane (DM12), Me(SiMe$_2$)$_{12}$Me, and DM6Cl were prepared in a similar manner to procedures described in literatures.[20,21] Permethyloligosilanes were purified by several recrystallizations. PDMS was commercially available from Nippon Soda Co. and was used without further purification. ^{1}H-NMR spectra of the oligosilanes in deuterated chloroform were measured using Bruker model AC-200 (200 MHz). Bio-Rad model FTS-60A FT-IR was used for infrared measurements. Samples were made into KBr pellets and subjected to the measurements. For Raman measurements, the samples were sealed in glass tubes, and spectra were recorded with Spex model 1877 Raman spectrometer using a 514.5 nm line of the argon ion laser as an excitation source.

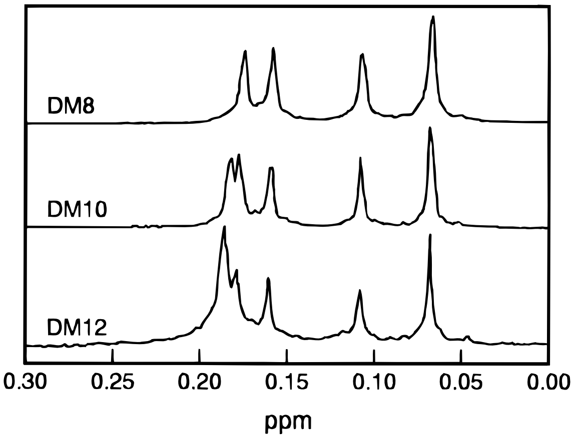


Figure 1. ^{1}H-NMR spectra of linear oligosilanes.

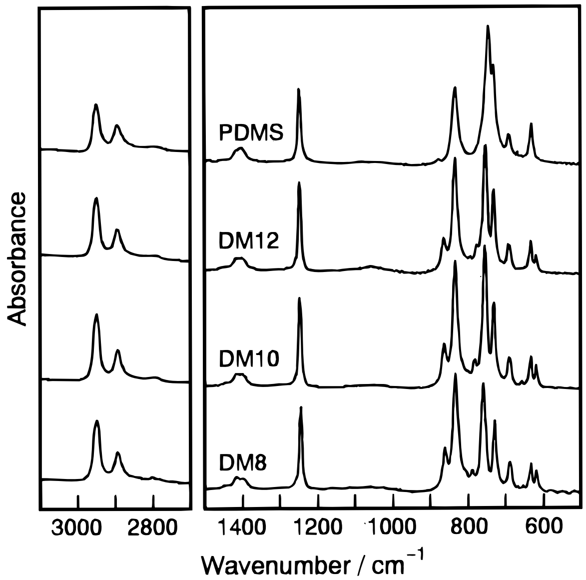
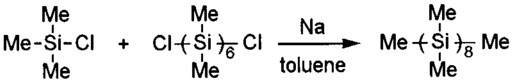


Figure 2. Infrared spectra of linear oligosilanes (KBr pellet).

Scheme 1



$$Me_3SiCl + Cl(SiMe_2)_6Cl \xrightarrow[\text{toluene}]{\text{Na}} Me(SiMe_2)_8Me$$

Figure 1 shows ^{1}H-NMR spectra of the permethyloligosilanes. Methyl groups closer to the chain end (0.07 ppm) showed resonance at higher field, and no unexpected peak was observed. This shows that the samples have no detectable contamination. Infrared spectra of the oligosilanes, along with that of PDMS, were reproduced in Figure 2. In an infrared spectrum of any compound synthesized by the Wurtz coupling, 1100−1000 cm^{-1} region has specific importance, because Si−O bonds can be easily introduced into silicon catenation during the reaction and Si−O shows strong absorption in the region. In the spectra of the oligosilanes and the polymer, only very small absorptions were observed in the Si−O region. This indicates that the oligosilanes contain negligible amount of Si−O contamination and are pure enough for the measurement of vibrational spectra. Bands at 863 and 618 cm^{-1} were not observed in the spectrum of PDMS, and these bands were stronger for an oligosilane of lower molecular weight. These bands were assigned to the end group, −SiMe$_3$. The other bands were almost the same as those of PDMS, and this suggests that the oligosilanes have almost the same chemical and conformational structure as PDMS. The authors have noticed that the 742.5 cm^{-1} band of PDMS shows a small shift toward higher wavenumbers in the spectra of oligosilanes, and details will be published elsewhere.

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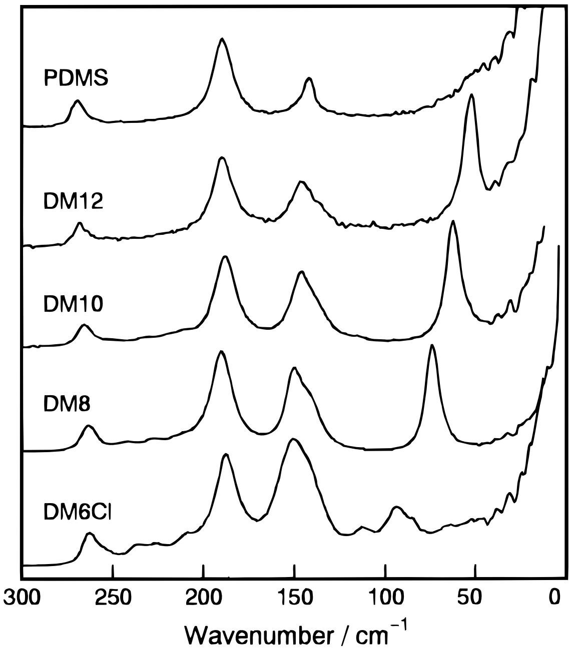

Figure 3. Raman spectra of linear oligosilanes and PDMS.

In the higher frequency region of Raman spectra of the oligosilanes, some additional bands were observed (*e.g.*, 862, 734, and 618 cm^{-1}). These new bands appear at the same frequency among the spectra and are stronger in the spectrum of lower molecular weight oligosilane. These new bands in the higher frequency region were assignable to the end group. Other Raman bands were observed at the same position with minor deviation. This also suggests that the oligosilanes have the same conformation as PDMS, *i.e.*, planar zig zag. Figure 3 shows a low-wavenumber region of Raman spectra of the oligosilanes and PDMS. In the region below 100 cm^{-1}, a sharp scattering was observed in the spectra of oligosilanes, while no line was found in the spectrum of PDMS. The new band cannot be attributed to impurities, because the oligosilane samples were pure enough. This band at the lower wavenumber region shows large molecular weight dependence among the oligosilanes; *i.e.*, in the spectrum of shorter oligosilane, the band appears at higher wavenumber. This behavior is characteristic of LAM bands, and these bands were assigned to LAM bands of the linear oligosilanes. In the case of PDMS, length of extended chains would be much longer than that in the oligosilanes and LAM bands would appear at much lower wavenumber, *i.e.*, too close to Rayleigh scattering to be observed.

To confirm this assumption, Young's modulus of each oligosilane was estimated using the uniform elastic rod model. LAM-*m* frequency, ν_m, can be written as $\nu_m^2 = (m/2L)^2 E/\rho$, where L, E, and ρ are the length, Young's modulus, and density of the rod, respectively. In this study, L (0.194 nm/unit) and ρ (1.022 g/cm^3) are estimated from the unit cell structure of PDMS,[22] and effects of the end groups on length and/or density were neglected for simplicity. Estimated Young's modulus, assuming that the band was LAM-1 modes, was shown in Table 1, along with observed wavenumbers and chain lengths used in the calculations. Deviations among the estimated values were due to the effect of end groups, *i.e.*, the methyl group (or chlorine). For comparison, a crystalline modulus of PDMS was roughly estimated by Treloar's method,[23] in which stretching of bonds and deformation of bond angles were treated independently. As Treloar's method gives a rough estimation, the force constants of Si−Si stretching and Si−Si−Si bending of Si_6Me_{12} (160 and 9 N/m, respectively)[24] were used instead of those of PDMS. An estimated crystalline modulus of PDMS was about 30 GPa. Treloar's method usually gives much smaller estimation than a precisely calculated value, *e.g.*, this method gave about 2/3 of a precisely calculated value in the case of polyethylene.[23,25] Thus, Young's modulus estimated from the wavenumber of the low-wavenumber Raman scattering of oligosilanes, around 50 GPa, was a reasonable value as the crystalline modulus of PDMS. This supports the assumption that the new Raman bands in a low-frequency region are LAM modes, and it also suggests the bands are LAM-1. LAM-3 and higher order modes were thought to be too weak to be observed and/or LAM-3 would be superimposed to the other bands at a higher wavenumber region. Thus, the LAM bands of oligosilane were first observed, and measurements of a series of oligosilanes of wider variety in length and a precise model would lead to a more reliable value of elastic modulus of PDMS.

Table 1. Estimated Young's Modulus of Linear Oligosilanes

sample	ν_1 (cm^{-1})	L (nm)	E (GPa)
DM6Cl	93	1.16	43.1
DM8	74	1.55	48.5
DM10	62.5	1.94	54.1
DM12	52.5	2.33	55.0

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