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Methyl Rocking Vibrational Modes of Poly(dimethylsilane)

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Introduction

Polysilanes are polymers containing only silicon in the main chain and having organic substituents. One of the most interesting properties of the polysilanes is their remarkable electronic absorption spectra.[1−3] Besides the electronic absorption, some polysilanes also show thermochromism, piezochromism, photoluminescence, conductivity, etc., and a number of new applications are expected.[4−12] As the electronic properties are attributed to σ-electron delocalization along main chains,[13−15] it is of interest to form well-oriented polysilane films, and methods such as vacuum-deposition, Langmuir−Blodgett film, and mechanical deposition have been applied to prepare the polysilane films.[16−29]

Poly(dimethylsilane) (PDMS), a simple representative of the polysilanes, is an important polymer in understanding the basic properties of polysilanes. Well-oriented films of PDMS have been prepared by the vacuum-deposition and the mechanical deposition methods.[18−24] Vibrational spectroscopy seems to be one of the important methods to characterize the oriented films, because it can be informative of chemical structure, conformation, and higher order structure as well as molecular orientation of the film. However, the orientations of the films of PDMS were measured by UV spectra and/or X-ray diffraction, so far. In order to apply vibrational spectroscopy to orientation studies, polarization, as well as assignment, of vibrational bands has to be known. Especially, bands of strong absorption are most important, because strong bands can be observed easier than other weaker bands. In the case of PDMS, Wesson *et al.* and Leites *et al.* reported vibrational spectra and assigned some bands; however, symmetry species or polarization of vibrational bands is far from completion and polarization of the strong bands in the infrared spectrum, *i.e.*, methyl rocking modes, was not clarified.[30,31]

A well-oriented sample is ideal to measure polarization of bands. Oriented thin films of PDMS can be prepared by the vacuum-deposition method under certain conditions; however, infrared spectrum of the film showed some degradation in molecular chains. High temperature during the evaporation process is thought to cause the degradation. Recently, it was found that well-oriented films of a linear oligosilane can be prepared by the vacuum-deposition method without degradation. In this study, vibrational spectra of well-oriented films of a dimethylsilane oligomer were measured and polarization of the bands was determined. Vibrational spectra of poly(methylethylsilane) (PMES) and other polysilanes were measured and compared with those of PDMS. Assignments of methyl rocking modes of the polymers were also discussed in relation with the polarization of the bands.

Experimental Section

PDMS was commercially available from Nippon Soda Co. and was used without further purification. PMES, poly(diethylsilane) (PDES) and copoly(dimethylsilane−diethylsilane) (co-P(DMS−DES)) were prepared by Wurtz coupling of methylethyldichlorosilane, diethyldichlorosilane, and a mixture (molar ratio 1:1) of dimethyldichlorosilane and diethyldichlorosilane, respectively. Permethyldodecasilane (DM12), Me(SiMe$_2$)$_{12}$Me, was prepared as published previously.[22]

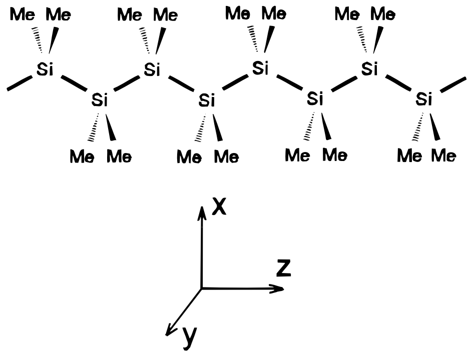

Figure 1. The coordinate in a PDMS molecule for the factor group analysis.

Oriented films of DM12 were prepared in a vacuum at less than 5×10^{-6} Torr with an apparatus for vacuum-deposition (Ayumi Kogyo model VE-88-11). DM12 powder was deposited to KBr and silver mirror for transmission and reflection−absorption infrared measurements, respectively. Bio-Rad model FTS-60A FT-IR was used for infrared measurements. Raman spectra were recorded with Spex model 1877 Raman spectrometer using a 514.5 nm line of argon ion laser as an excitation source.

Results and Discussion

PDMS chains were thought to be planar zig-zag conformation and an infinite chain is isomorphous with the point group D_{2h}. Symmetry species of methyl rocking modes are Raman-active A_g, B_{1g}, B_{2g}, B_{3g}, infrared-active B_{1u}, B_{2u}, B_{3u}, and inactive A_u. (Coordinates are shown in Figure 1.) Thus, three bands, one parallel band and two perpendicular bands, are expected in an infrared spectrum. Figure 2 (top) shows the infrared spectrum of PDMS powder (KBr pellet, random orientation). In an 850−700 cm^{-1} region, *i.e.* methyl rocking region, three bands were observed at 832, 742.5, and 731 cm^{-1}. The 832 and 742.5 cm^{-1} bands were already assigned to methyl rocking modes, however, the 731 cm^{-1} band has not been reported in the literature.[30,31] It is reasonable to assign the 731 cm^{-1} band as the third methyl rocking mode.

In order to determine the polarization of these infrared bands, a well-oriented sample is necessary. In a vacuum-deposited film of PDMS, molecules were aligned normal to substrate under certain deposition conditions; however, some degradation of polymer chains was unavoidable due to high temperature during the evaporation process.[21,22] In this study, vacuum-deposited films of DM12 were used instead. The oligomer can be evaporated at much lower temperature than the polymer, and the well-oriented film can be prepared without degradation of molecules. Molecules in the film were oriented normal to substrate, and the orientation was confirmed by X-ray diffraction and UV spectra.[22] Infrared spectra of vacuum-deposited DM12 films in normal transmission and reflection−absorption alignment were reproduced in Figure 3. In the reflection−absorption alignment, the electric field is perpendicular to the substrate when an incident angle (86° in this study) is close to the grazing angle. On the other hand, the electric field is parallel to the substrate in the

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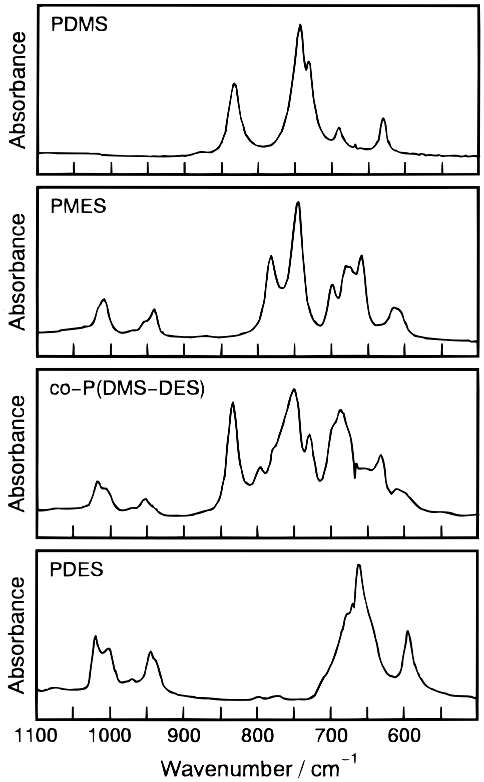

Figure 2. Infrared spectra of PDMS, PMES, and other polymers. (KBr pellet)

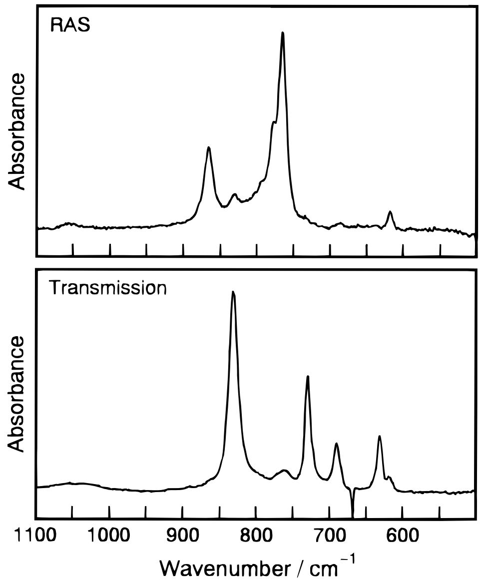

Figure 3. Infrared spectra of vacuum-deposited oriented films of DM12.

transmission alignment. As the molecules in the films are oriented perpendicular to the substrate, only parallel bands should be observed by the reflection–absorption method (Figure 3, top) and perpendicular bands should appear in a transmission spectrum (Figure 3, bottom). Bands at 862 and 618 cm^{-1} were characteristic of the oligomer and are due to the end group. Minor deviations in wavenumber were found, and details will be published elsewhere. The result clearly shows that the 742.5 cm^{-1} band of PDMS is the parallel band and 832 and 731 cm^{-1} bands are perpendicular bands. The parallel band at 742.5 cm^{-1} was assigned to B_{1u} mode, in which methyl groups rock parallel to the chain axis. The perpendicular bands of PDMS at 832 and 731 cm^{-1} were thought to be B_{3u} and B_{2u} modes, where two methyl groups bonded to a silicon atom rock perpendicular to the chain axis. It should be noted that two methyl groups rock symmetrically in the case of B_{3u} and antisymmetircally in the case of B_{2u}.

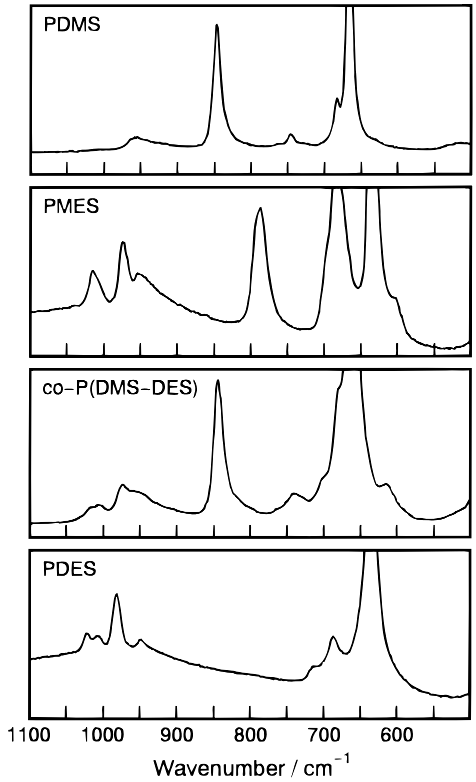

Figure 4. Raman spectra of PDMS, PMES, and other polymers.

In order to obtain additional information, infrared spectra of PMES were investigated. As PMES has only one methyl group on each silicon atom, two perpendicular methyl rocking modes are expected to become one mode, and two methyl rocking modes, one is parallel and the other is perpendicular to the *c*-axis, are expected in an infrared spectrum. Infrared spectra of PDES and co-P(DMS–DES) were also measured for comparison. Figure 2 shows the infrared spectra (KBr pellet, random orientation) of PDMS, PMES, PDES, and co-P(DMS-DES). In the 900–700 cm^{-1} region of the spectrum of PDES, no significant absorption was observed, *i.e.*, ethyl groups have no absorption in the region and bands in this region are due to methyl groups. In the spectrum of PMES, two bands (782.5 and 745.5 cm^{-1}) were observed in this region. One appears at almost the same frequency as the parallel methyl rocking mode (B_{1u}) of PDMS. The other band appears between the frequencies of two perpendicular bands (B_{2u} and B_{3u}) of PDMS. It is natural to assign the band at 745.5 cm^{-1} to methyl rocking parallel to the *c*-axis and the band at 782.5 cm^{-1} to methyl rocking perpendicular to the *c*-axis. In the spectrum of co-P(DMS–DES), three bands were observed at almost the same frequencies as those of PDMS. This also suggests that the separation of the two perpendicular rocking modes (B_{2u} and B_{3u}) are due to the interaction between two methyl groups bonding to the same silicon atom.

Raman spectra of the polymers were also measured and are shown in Figure 4. As was found in the infrared spectrum of PDES, no significant peak was observed in the methyl rocking region (850–700 cm^{-1}) of the Raman

Table 1. Observed Wavenumber and Assignment of Methyl Rocking Modes of PDMS

compound	species	polarization	wavenumber/cm^{-1}		rocking direction
			infrared	Raman	
PDMS (D_{2h})	A_g		inactive	846	⊥
	B_{1g}		inactive	746	⊥
	B_{2g}		inactive		∥
	B_{3g}		inactive		∥
	B_{1u}	∥	742.5	inactive	∥
	B_{2u}	⊥	731	inactive	⊥
	B_{3u}	⊥	832	inactive	⊥
	A_u		inactive	inactive	∥
PMES			745.5		∥
			782.5		⊥
				790	⊥

spectrum of PDES, and peaks in this region are due to methyl groups. In this region, PDMS gave two Raman peaks (846 and 746 cm^{-1}) and PMES showed only one Raman peak (790 cm^{-1}). It is assumed that the 790 cm^{-1} peak of PMES was split into two peaks of PDMS due to the interaction between two methyl groups bonding to the same silicon atom. Possible combinations of symmetry species for the two split peaks are A_g and B_{1g} (perpendicular methyl rocking) or B_{2g} and B_{3g} (parallel methyl rocking). A_g and B_{1g} pair seems to be favorable, because perpendicular rocking modes showed large splitting in the case of infrared spectrum of PDMS. Usually, the totally symmetric mode, *i.e.*, A_g, gives a very strong Raman scattering, and it is unlikely that B_{2g} and B_{3g} modes are observed while A_g and B_{1g} modes are too weak to be observed. Thus, the A_g and B_{1g} pair was assigned to the two peaks of PDMS, and the stronger peak at 846 cm^{-1} was assigned to totally symmetric A_g (symmetric rocking, perpendicular) and the other peak at 746 cm^{-1} to B_{1g} (antisymmetric rocking, perpendicular). It is reasonable to assign the infrared band at 832 cm^{-1} to be B_{3u} (symmetric rocking, perpendicular) which corresponds to A_g, and the band at 731 cm^{-1} to be B_{2u} (antisymmetric rocking, perpendicular) which corresponds to B_{1g}. Assumed assignments of methyl rocking modes were summarized in Table 1. The Raman spectrum of co-P(DMS−DES) in the region was almost the same as that of PDMS. This also supports the discussion above.

Conclusion

It was found that methyl rocking bands in the infrared spectrum of PDMS consist of three bands, (B_{1u}, B_{2u}, and B_{3u}). Polarization of three bands was determined using well-oriented thin films of DM12. The assignment was also confirmed through observation of the infrared spectrum of PMES, where two methyl rocking bands were observed. In Raman spectrum of PDMS, two bands out of four Raman active modes were observed. Symmetry species of methyl rocking bands of PDMS were proposed.

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