*Macromolecules* **1998,** *31,* 7483−7487

# Infrared Spectroscopic Studies on the Molecular Orientation of Vacuum-Deposited Thin Films of Poly(dimethylsilane) and a Linear Oligosilane

**Masaki Shimomura,* Hajime Okumoto, Akira Kaito, and Katsuhiko Ueno**

*National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

**Jingshu Shen**

*Institute of Chemistry, Academia Sinica, Haidian, Beijing, China*

**Kohzo Ito**

*Graduate School of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*

*Received February 13, 1998; Revised Manuscript Received July 17, 1998*

ABSTRACT: Thin films of poly(dimethylsilane) (PDMS) and permethyldodecasilane (DM12) were prepared by the vacuum-deposition method, and the molecular orientation in the films was investigated. Well-oriented films of DM12 were prepared without detectable degradation; however, degradation occurred in the films of PDMS, though well-oriented films were also obtained. Infrared and UV spectra of the vacuum-deposited films were measured with inclined sample alignment. In the spectra of films deposited to substrates at room temperature, a methyl rocking (parallel) band and a sharp UV absorption, which have the same polarity parallel to the chain axis, became stronger when the samples were inclined. Both of the absorptions also showed large dichroism when the samples were inclined. These results suggest that the PDMS and DM12 molecules in the films were oriented perpendicular to the substrate. The infrared spectra of vacuum-deposited PDMS films show Si−H and Si−O bonds formation; *i.e.*, PDMS molecules were degraded during the deposition process. In clear contrast, the infrared spectra of the vacuum-deposited films of DM12 showed no molecular degradation.

## Introduction

Polysilanes are polymers containing only silicon atoms in the backbone and having hydrocarbon substituents. Poly(dimethylsilane) (PDMS) was reported in 1949;[1] however, the polymer attracted little scientific interest because of its insolubility and intractability. In the 1970s, polysilanes attracted interest as the precursor of silicon carbide fiber,[2] and polysilanes evoked considerable scientific interest since the synthesis of soluble substituted polysilanes in the 1980s. One of the most interesting properties of polysilanes is their remarkable electronic absorption spectra.[3−5] These polymers have UV absorption bands, which resulted from the $\sigma$-electron delocalization along the main chain.[6−8] Besides the electronic absorption, some polysilanes also show thermochromism, piezochromism, photoluminescence, photodegradation, conductivity, etc., and a number of new applications are expected.[9−14] Modern interest in polysilanes is generated by these unique electronic properties, which are attributed to $\sigma$-electron delocalization along main chains. It is of interest to form well-oriented polysilanes films, which are expected to have anisotropic electronic properties.[15−17] The vibrational spectroscopy is one of the most important methods to characterize oriented films, because it can give information on chemical structures, etc., as well as molecular orientation. Though studies on the vibrational spectroscopy of polysilanes have been done,[11,13,18−20] most studies on oriented polysilanes have been done with UV spectra and X-ray diffraction.

The vacuum deposition has been considered as one of powerful methods to form organic thin films, and a number of studies have been done with vacuum-deposited organic films.[21−24] It is well-known that vacuum-deposited organic thin films show various properties depending on the deposition condition, such as temperatures of substrate and furnace, substrate, deposition rate, etc. PDMS is a simple representative of the polysilanes, and it is an important polymer to understand basic properties of polysilanes. However, the insolubility of PDMS makes it difficult to characterize, to utilize the polymer as materials, or to make PDMS thin films.[25] Recently, a vacuum-deposition method has been used to prepare oriented thin films of PDMS by the authors[26,27] and Furukawa *et al.*[28−31] The molecular orientation of the films was examined using UV absorption spectra with an inclined sample alignment in relation to temperature of substrates during vacuum-deposition.[26] UV and HPLC measurements, however, suggest that cleavage of the Si−Si bonds of PDMS was unavoidable due to the high furnace temperature during the vacuum-deposition.

Linear oligosilanes, $Me(SiMe_2)_nMe$, of well-defined molecular weight and chemical structure are very important as analogues of PDMS.[14,19,27,32,33] In clear contrast to PDMS, the oligosilanes usually have melting points without decomposition, and they are expected to be vacuum-evaporated under milder conditions than those for PDMS. It was expected that cleavage of Si−Si bonds or other degradation of molecules would not occur. Previously, thin films of permethyldodecasilane (DM12) were prepared by the vacuum-deposition method, and molecular orientation was confirmed by UV spectra with the inclined sample alignment and wide-angle X-ray diffraction.[27]

10.1021/ma980235j CCC: $15.00

In this study, vacuum-deposited thin films of PDMS and DM12 were prepared, and their molecular orientation was measured by infrared and UV measurements. Changes in the chemical structure of the PDMS and DM12 films, which were difficult to detect by UV or X-ray diffraction measurements, were also examined by infrared spectroscopy and were discussed in relation with their thermal stability during the vacuum-deposition.

## Experimental Section

PDMS powder, which was commercially available from Nippon Soda Co., was used as an evaporation source without further purification. DM12 was kindly provided by Dr. Tetsuo Yatabe.[27] Vacuum-deposited films of PDMS and DM12 were prepared with an apparatus for vacuum deposition (Ayumi Kogyo model VE-88-11). The samples were vacuum-deposited to various substrates, e.g., quartz glass plates, KBr and CsI windows, and vacuum-deposited silver mirrors in a vacuum at $5 \times 10^{-5}$−$5 \times 10^{-6}$ Torr. The furnace temperature was 400 °C in the case of PDMS and 125−130 °C in the case of DM12. Typical deposition time, 20 min, resulted in a film of about 200 nm thickness (estimated by a thickness monitor with a quartz oscillator).

The infrared spectra were measured with Perkin-Elmer model 1800 and Bio-Rad model FTS-60A FT-IRs. Nominal resolution was 1 or 2 $cm^{-1}$, and 64−1000 scans, which depend on sample thickness, sample alignment, and measuring methods, resulted in spectra of enough signal-to-noise ratio. Transmission spectra of vacuum-deposited films (on KBr or CsI windows) were measured in the usual alignment (beam incidents normal to the surface) and inclined sample alignments, where samples were placed with various inclination angles to the incident beam. A vacuum-deposited film of DM12 on a silver mirror was subjected to the reflection−absorption measurement (RAS). Powder samples were made into KBr pellets and subjected to the measurements. Backgrounds due to the variation of water vapor concentration in the spectrometer were removed using the spectral subtraction technique. Japan Spectroscopic Co. model Ubest-55 spectrometer was used for the UV measurements. The UV spectra of the vacuum-deposited films were measured in the usual alignment and in inclined sample alignments.

## Results and Discussion

**A. Vacuum-Deposited Films of PDMS.** Infrared spectra, which are very informative on the structure of vacuum-deposited PDMS films, were examined. PDMS was vacuum-deposited to CsI and KBr windows for infrared measurements. Figure 1 reproduces the infrared spectra of vacuum-deposited PDMS films on CsI at room temperature (B) and at low temperature (C). An infrared spectrum of PDMS before the vacuum-deposition measured by KBr pellet method was also shown in Figure 1A. Infrared spectra of the films on KBr windows were almost the same as those of the films on CsI windows. In the infrared spectra of vacuum-deposited PDMS films, new bands appeared and a band at 760 $cm^{-1}$ became very weak, which is the strongest absorption of the PDMS powder. Among the new bands, a band around 2090 $cm^{-1}$ is due to Si−H stretching and bands in the 1100−1000 $cm^{-1}$ region are of Si−O bonds. Bands in the 900−700 $cm^{-1}$ region were not readily assignable; however, these might be due to Si−C−Si bonds resulted from cleavage of Si−Si bonds and recombination, which also forms Si−H bonds, during the vacuum evaporation. The infrared spectrum of the PDMS powder left in the furnace after the vacuum-deposition was also measured by the KBr pellet method. The spectrum was essentially the same as that of PDMS before evaporation, where Si−H formation was not observed and a small amount of Si−O formation was found. This indicates that the Si−H and Si−O formation occurred during and/or after molecules evaporated, and not in the furnace, which was kept at lower temperature than that of the silicon carbide production.

Infrared spectra of a PDMS film vacuum-deposited on a KBr substrate at room temperature were also measured with various sample inclination angles, $\theta$, as shown schematically in Figure 2. The spectra were reproduced in Figure 3, where the band at 760 $cm^{-1}$ was weak in the spectrum of normal alignment and intensity of the band increased as the sample inclination angle became large. The 760 $cm^{-1}$ band is assigned to methyl

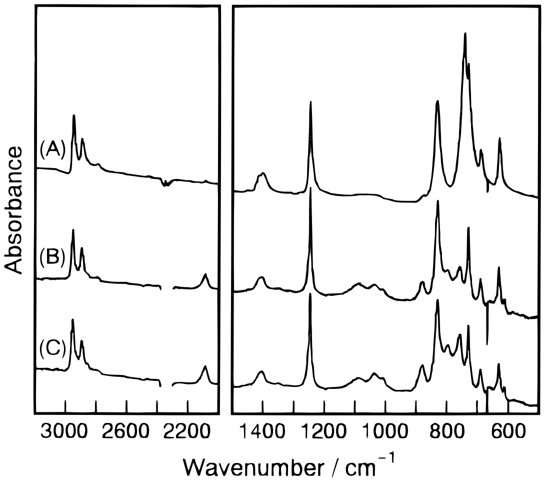

**Figure 1.** Infrared spectra of PDMS: (A) before the vacuum-deposition; (B) deposited to a CsI window at room temperature; (C) deposited to a CsI window at −150 °C.

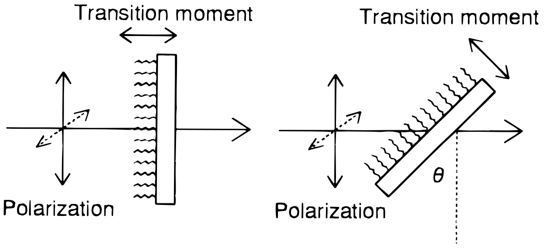

**Figure 2.** Schematic illustration of PDMS and DM12 molecules in vacuum-deposited films.

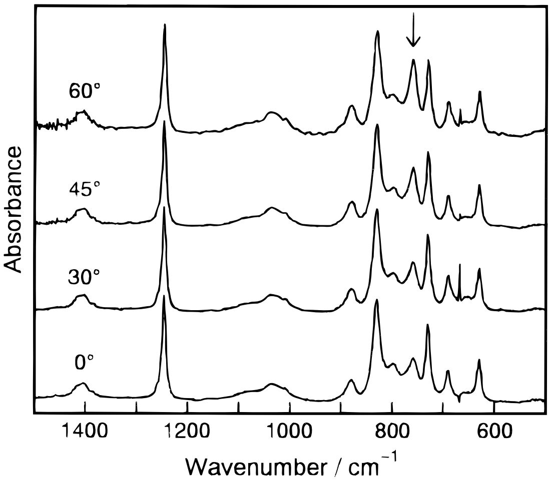

**Figure 3.** Infrared spectra of PDMS deposited to a KBr window at room temperature with various sample inclination angles.

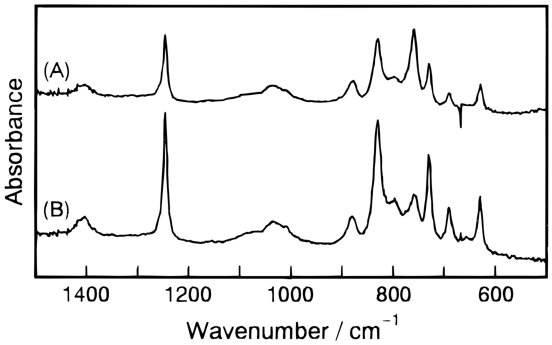

**Figure 4.** Infrared dichroism of PDMS deposited to a KBr window at room temperature in a 60° inclined sample alignment.

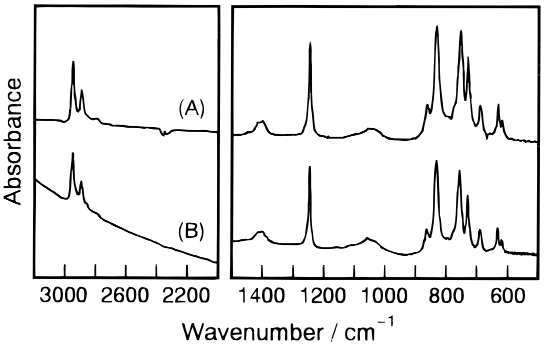

**Figure 5.** Infrared spectra of DM12: (A) before the vacuum-deposition; (B) after the vacuum-deposition (random orientation).

rocking parallel to the chain axis[20] and has the induced dipole moment parallel to the chain axis. The results can be interpreted in terms of molecular orientation of PDMS in the vacuum-deposited films, as follows. If the main chains align perpendicular to the substrate (Figure 2, left), no absorption should occur with the normal incident beam, because the electric field is perpendicular to the chain axis and the induced dipole moment of the 760 cm$^{-1}$ band. With the inclined-sample alignment, however, the absorption can be observed (Figure 2, right), because the main chains are not perpendicular to the electric field of the incident beam. An infrared dichroism of the film was also measured with 60° inclined sample alignment. The electric field of polarized light shown by the solid arrow in Figure 2 is not perpendicular to the oriented PDMS main chains when the sample was inclined, and the 760 cm$^{-1}$ band is expected to become strong. The electric field of the polarized light shown by the broken arrow is always perpendicular to the main chain even though the sample was inclined, and the absorption will not be observed. The polarized infrared spectra of the vacuum-deposited PDMS film are reproduced in Figure 4A,B, which corresponds to the polarized incident light shown by the solid and broken arrows, respectively. As expected, the 760 cm$^{-1}$ band is much stronger in Figure 4A than in Figure 4B. Thus, it was confirmed by the infrared measurements that the major parts of vacuum-deposited PDMS molecules were oriented perpendicular to the substrate. However, small parts of PDMS may not be in perpendicular orientation, because the 760 cm$^{-1}$ band appears even in the normal sample alignment.

UV spectra of the vacuum-deposited films of PDMS are of particular interest, and spectra of the PDMS films were also measured with various inclined-sample alignments in order to determine molecular orientation of the films.[26] It was concluded that the PDMS molecules were oriented perpendicular to the substrate in the films deposited to the substrate at room temperature, as shown schematically in Figure 2. On the other hand, no particular orientation was found when PDMS was vacuum-deposited to a cooled substrate. It was assumed that the temperature of substrates is a major factor that affects the structure of vacuum-deposited PDMS films.[26]

The methyl rocking band (parallel) of vacuum-deposited films of PDMS (760 cm$^{-1}$) appeared at higher wavenumber than that of PDMS powder (742.5 cm$^{-1}$). Though the mechanism is not clear so far, the methyl rocking (parallel) band of oligomeric analogues of PDMS show molecular weight dependence, and a shorter oligosilane gave the band at higher wavenumber region.[19] The shift of the methyl rocking band of the vacuum-deposited PDMS toward higher wavenumber region qualitatively indicates that the molecules in the film have shorter Si catenation than the PDMS polymer. The UV absorption band also indicated that the molecules have shorter catenation. The Si−H stretching band, Si−O bands, and bands in the 900−700 cm$^{-1}$ region, which might be attributed to Si−C−Si bonds, of vacuum-deposited films of PDMS clearly indicate that the molecules degraded during the deposition process. Complicated molecular degradation is inevitable because of the severe condition necessary to evaporate PDMS molecules, though the PDMS films of perpendicular orientation can be prepared by the vacuum-deposition method.

**B. Vacuum-Deposited Films of DM12.** Previously, vacuum-deposited films of DM12 was prepared by the authors.[27] The chemical structure of molecules in a vacuum-deposited DM12 film was examined by infrared measurements, because some degradation was found in the case of vacuum-deposited PDMS films. DM12 was vacuum-deposited to a KBr window, and the film was scraped off and made into a KBr pellet in order to make a random oriented sample. The infrared spectrum of the pellet was compared with that of DM12 before the vacuum-deposition. Both spectra were reproduced in Figure 5. The relative intensities of the bands did not vary between both spectra, and Si−O bonds (1100−1000 cm$^{-1}$ region) did not increase during the vacuum-deposition, though a small amount of Si−O bonds was found in both spectra. The clear 2100 cm$^{-1}$ region indicates that a detectable amount of Si−H bond formation and accompanying Si−C−Si bond formation, which may give rise to additional bands in the 900−700 cm$^{-1}$ region, did not occur. No shift of the methyl rocking (parallel) band (753 cm$^{-1}$), which shows molecular weight dependence, was observed, and Si−Si cleavage did not occur during the deposition. Thus, the infrared spectra show that DM12 can be vacuum-deposited without molecular degradation, in clear contrast to the case of PDMS.

DM12 was vacuum-deposited to quartz plates at room temperature and at low temperature (−150 °C) and subjected to UV measurements. Figure 6 (left) shows UV spectra of the film deposited to a substrate at room temperature measured with various sample inclination angles, $\theta$. Behavior of the 285 nm band with parallel polarity indicates that the molecules were oriented perpendicular to the substrate. UV dichroism of the band was also measured in the inclined sample alignment (Figure 6, right). Large dichroism of the band

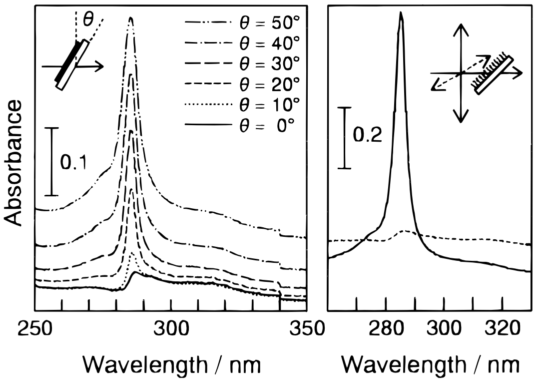

**Figure 6.** UV spectra of a vacuum-deposited DM12 film on a quartz plate at room temperature (left) and UV dichroism of the film in 45° inclined sample alignment (right).

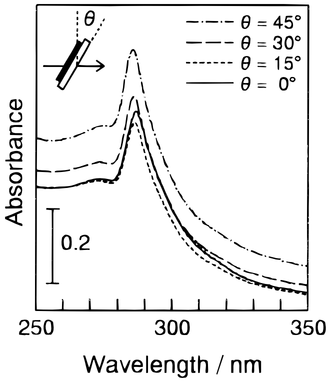

**Figure 7.** UV spectra of a vacuum-deposited DM12 film on a quartz plate at low temperature.

supports the perpendicular orientation of DM12 in the film as was discussed with the vacuum-deposited films of PDMS, because the UV band has the same polarity as infrared parallel bands. The UV spectra of a DM12 film vacuum-deposited to a cooled substrate with various sample inclination angles are shown in Figure 7. The intensity of the band did not vary much with inclination angles, and the DM12 molecules have no significant orientation when vacuum-deposited to a cooled substrate. Thus, it is concluded that the temperature of a substrate is a major factor which affects molecular orientation of DM12 vacuum-deposited films.

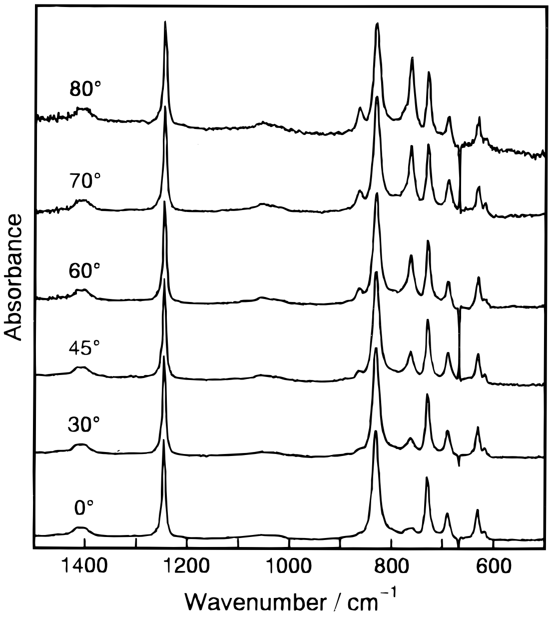

**Figure 8.** Infrared spectra of DM12 deposited to a KBr window at room temperature with various sample inclination angles.

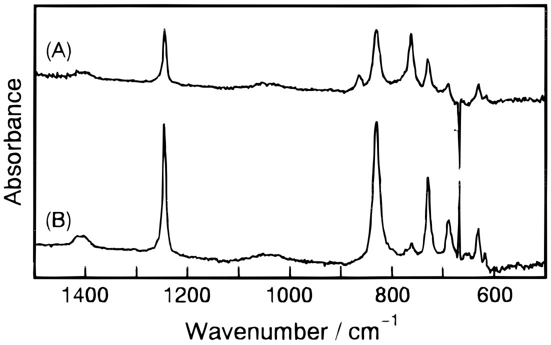

**Figure 9.** Infrared dichroism of DM12 deposited to a KBr window at room temperature in 60° inclined sample alignment.

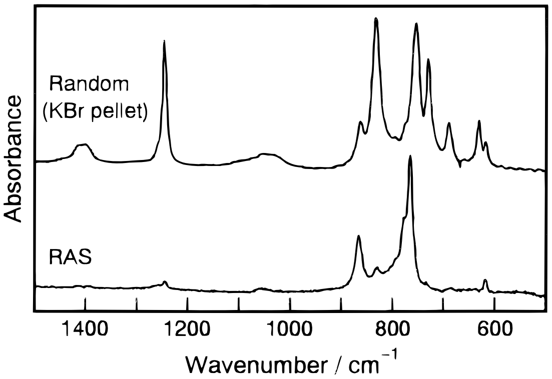

**Figure 10.** Infrared reflection−absorption spectrum of vacuum-deposited DM12 films.

Infrared spectra of a DM12 film vacuum-deposited on a KBr substrate at room temperature were measured at various sample inclination angles, and the spectra were reproduced in Figure 8. Bands at 862 and 753 cm$^{-1}$ almost disappear with the normal sample alignment, and intensities of these bands increased at large sample inclination angles. The 753 cm$^{-1}$ band is assigned to methyl rocking (parallel) mode, which has the transition dipole moment parallel to the chain axis, and the band at 862 cm$^{-1}$ would be of the end groups (Si−Me$_3$). Infrared dichroism of the film was also measured with 60° inclined sample alignment. The spectrum measured by the polarized light indicated in the solid line in Figure 2 shows strong absorptions of 862 and 753 cm$^{-1}$ bands (Figure 9A). In a spectrum measured with the light shown with the broken line in Figure 2, however, both bands almost disappear (Figure 9B). These behaviors of the parallel band at 753 cm$^{-1}$ can be interpreted in terms of perpendicular orientation of DM12 molecules, as described in the case of the PDMS film. An infrared spectrum of the DM12 film deposited to a silver mirror at room temperature was measured by RAS.[34] 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. If the molecules in the films are oriented perpendicular to the substrate, only parallel bands should be observed by the reflection−absorption method. In Figure 10, the RAS spectrum (bottom) was compared with the spectrum of random oriented DM12 in a KBr pellet (top). In the RAS spectrum, only the

753 $cm^{-1}$ band with parallel polarization and bands due to the end group (862 and 618 $cm^{-1}$) appear and perpendicular bands are almost absent as expected. These infrared spectra clearly showed that the DM12 molecules in the vacuum-deposited films were oriented perpendicular to the substrate.

## Conclusion

It was found that perpendicular oriented thin films of PDMS and DM12 on various substrates can be prepared by the vacuum-deposition method. Infrared and UV spectra measured with the inclined sample alignment show that the molecules in the vacuum-deposited films are oriented normal to the substrate, when the films were deposited to the substrate at room temperature during the vacuum-deposition. Dichroism of the films also supports the perpendicular orientation. In contrast, vacuum-deposited films show no significant orientation, if the substrates were kept at low temperature. Temperature of the substrate is the major condition that determines molecular orientation of the vacuum-deposited films of PDMS and DM12. The vacuum-deposition method is the one and only technique to make perpendicular oriented films of polysilanes and their analogues so far, and characteristic properties due to $\sigma$-electron delocalization were expected to appear specifically in the direction perpendicular to the film surface. The infrared spectra of vacuum-deposited PDMS films show that the film was made of PDMS of short chain length with Si−H, Si−O, and Si−C−Si bonds, i.e., degraded molecules. In clear contrast, no degradation of molecules was detected in the vacuum-deposited DM12 films, and the importance of oligosilanes as analogues of polysilanes was clearly demonstrated. Infrared measurement can detect changes in chemical structure of vacuum-deposited thin films, as well as molecular orientation, and infrared spectroscopy was found to be important in studies of vacuum-deposited thin films of polysilanes.

**Acknowledgment.** Thanks are due to Dr. Tetsuo Yatabe of National Institute of Materials and Chemical Research for providing the DM12 sample.

## References and Notes

(1) Burkhard, C. A. *J. Am. Chem. Soc.* **1949**, *71*, 963.
(2) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**, *13*, 2569.
(3) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369.
(4) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471.
(5) Trefonas, P., III.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.
(6) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.
(7) Kepler, R. G. *Synth. Met.* **1989**, *28*, C573.
(8) Zeigler, J. M. *Synth. Met.* **1989**, *28*, C581.
(9) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(10) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(11) Rabolt, J. F.; Hofer, D.; Miller, R. D. *Macromolecules* **1986**, *19*, 611.
(12) Matsumoto, N. *Kotai Butsuri* **1987**, *22*, 907.
(13) Song, K.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1993**, *26*, 3232.
(14) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19.
(15) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Wilson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.
(16) Kani, R.; Nakano, Y.; Hayase, S. *Macromolecules* **1995**, *28*, 1773.
(17) Yoshida, M.; Nakanishi, F.; Seki, T.; Sakamoto, K.; Sakurai, H. *Macromolecules* **1997**, *30*, 1860.
(18) Leites, L. A.; Bukalov, S. S.; Yadritzeva, T. S.; Mokhov, M. K.; Antipova, B. A.; Frunze, T. M.; Dement'ev, V. V. *Macromolecules* **1992**, *25*, 2991.
(19) Shimomura, M.; Yatabe, T.; Kaito, A.; Tanabe, Y. *Macromolecules* **1997**, *30*, 5570.
(20) Shimomura, M.; Kyotani, H.; Kaito, A. *Macromolecules* **1997**, *30*, 7604.
(21) Dahlberg, S. C.; Reinganum, C. B. *J. Chem. Phys.* **1982**, *76*, 2731.
(22) Hayashida, S.; Sato, H.; Sugawara, S. *Jpn. J. Appl. Phys.* **1985**, *24*, 1436.
(23) Yoshida, T.; Morinaka, A.; Funakoshi, N. *Thin Solid Films* **1988**, *162*, 343.
(24) Ito, K.; Shimomura, M.; Kyotani, H.; Tanabe, Y. *Jpn. J. Appl. Phys.* **1992**, *31*, L106.
(25) (a) Recently, oriented films of PDMS were prepared by the mechanical deposition method. (b) Tanigaki, N.; Yase, K.; Kaito, A. *Thin Solid Films* **1996**, *273*, 263.
(26) Shimomura, M.; Ueno, K.; Okumoto, H.; Shen, J.-S.; Ito, K. *Macromolecules* **1994**, *27*, 7006.
(27) Yatabe, T.; Shimomura, M.; Kaito, A. *Chem. Lett.* **1996**, 551.
(28) Furukawa, S.; Obana, M.; Nakamine, T.; Shirakawa, Y.; Sorai, A.; Tamura, M. *J. Phys.: Condens. Matter* **1992**, *4*, 5167.
(29) Furukawa, S.; Takeuchi, K.; Nomura, T.; Yasuda, T.; Tamura, M. *J. Phys.: Condens. Matter* **1993**, *5*, 4729.
(30) Takeuchi, K.; Mizoguchi, M.; Kira, M.; Shimana, M.; Furukawa, S.; Tamura, M. *J. Phys.: Condens. Matter* **1994**, *6*, 10705.
(31) (a) Kakeuchi, K.; Furukawa, S. *Jpn. J. Appl. Phys.* **1995**, *34*, L195. (b) Kakeuchi, K.; Furukawa, S. *J. Phys. D: Appl. Phys.* **1995**, *28*, 535.
(32) Mazieres, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682.
(33) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345.
(34) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.

MA980235J