Molecular Orientation of Vacuum-Deposited Thin Films of Poly(dimethylsilane)

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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] These polymers with σ-bonded main chains show optical absorption in the UV region. It is believed that this results from σ-electron delocalization along the main chain.[4-6] Besides the electronic absorption, some polysilanes also show thermochromism, piezochromism, photoluminescence, photodegradation, conductivity, etc., and a number of new applications are expected.[7-15] Modern interests in polysilanes are generated by these unique electronic properties. As the electronic properties are attributed to σ-electron delocalization along the main chains, it is of interest to form well-oriented polysilanes.

Vacuum deposition has been of interest as a method to form thin films. The method has been utilized to form inorganic and metallic thin films in various fields. Recently, the vacuum-deposition method has been considered as one of the powerful methods to form organic thin films, and a number of studies have been done with vacuum-deposited organic films.[16-21] It is well known that vacuum-deposited organic thin films show different structures or properties depending on the deposition conditions, such as the temperatures of the substrate and furnace, kind of substrate, deposition rate, etc. Poly(dimethylsilane) (PDMS) is a simple representative of the polysilanes and it is an important polymer to understand the 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. In this study, the vacuum-deposition method was adopted to form thin films of PDMS, and the molecular orientation of the vacuum-deposited films will be discussed in relation with their UV spectra.

PDMS powder, which was commercially obtained from Nippon Soda Co., was used as an evaporation source without further purification. PDMS films were prepared with an apparatus for vacuum deposition (Ayumi Kogyo Model VE-88-11). The PDMS powder was heated in a quartz furnace around 400 °C and deposited on quartz plates for the UV measurements. A thickness monitor with a quartz oscillator was used to monitor the rate of the vacuum deposition and the amount of deposited films. PDMS was vacuum-deposited on the substrates at room temperature in a vacuum of less than 5×10^{-5} Torr, and the vacuum depositions on liquid-nitrogen-cooled substrates (−150 °C) were performed in a vacuum of less than 5×10^{-6} Torr. A Japan Spectroscopic Co. Model Ubest-55 spectrometer was used for the UV measurements. UV spectra of the vacuum-deposited films were measured in the usual alignment and in an alignment with an inclined sample. The spectra will be discussed in relation with the molecular orientation of the films.

Furukawa *et al.* reported that a sharp absorption was observed in a UV spectrum of vacuum-deposited PDMS film. They explained the absorption as being due to an excitonic excitation.[20] In a previous work,[22] a sharp peak at 296 nm was also observed in the UV spectrum of a PDMS film deposited on a quartz plate cooled to around −150 °C as reproduced by a solid line in Figure 1. However, in the spectrum of a PDMS film deposited on a quartz plate at room temperature, the 296 nm peak almost disappeared (Figure 2, solid line). The vacuum-deposited films can be resolved in hexane or tetrahydrofuran. In the UV spectra of the vacuum-deposited molecules in solution, the 296 nm absorption was not observed, and the difference in the UV spectra of as-deposited films was attributed to the difference in the higher-order structure of the films. GPC showed the molecular weight of the deposited PDMS is about 4×10^3. Infrared spectra of the films indicated formation of a small amount of Si–H and Si–O bonds; however, a certain length of Si catenations is thought to exist, which gave rise to the UV absorption.[22]

To obtain further information about the 296 nm absorption, the UV spectra of the PDMS films were measured with inclined-sample alignments (inclination angle 0–50°). The UV spectra of the PDMS film vacuum-deposited on a quartz plate at −150 °C are shown in Figure 1 along with a schematic illustration of the inclined-sample alignment. Here, no significant change was found in the spectra measured at different inclination angles. The UV spectra of a PDMS film deposited on a substrate at room temperature were also measured with the inclined-sample alignment and are shown in Figure 2. In contrast to the result shown in Figure 1, the intensity of the 296 nm absorption became stronger when the film was measured in an alignment of larger inclination angle.

These results can be interpreted in terms of molecular orientation of PDMS in the vacuum-deposited films. Most of the main chains of the PDMS molecules in the film deposited on a quartz plate at room temperature were assumed to be oriented perpendicular to the plate surface as shown schematically in Figure 3. Since UV absorptions of polysilanes are generally attributed to the σ-electron delocalization along the main chains, no absorption should occur with the normal incident beam if the main chains align perpendicular to the substrate (Figure 3, top). With the inclined-sample alignment, however, absorption due to the main chains can be observed (Figure 3, bottom), because the main chains are not perpendicular to the electric field of the incident beam. No significant orientation was assumed with the film deposited to a cooled substrate, and the absorption is always observed without significant change.

The dichroism of the 296 nm peak in the UV spectrum of PDMS film deposited on a substrate at room temperature was measured with 45° inclination (Figure 3, bottom). The UV spectra were measured using polarized light as shown by the solid and broken arrows in Figure 3. Here, the electric field of the polarized light shown by the solid arrow is not perpendicular to the oriented PDMS main chains, and the 296 nm absorption is expected to be observed. The electric field of the polarized light shown by the broken arrow is still perpendicular to the main chain and no absorption is expected. The polarized UV spectra of the vacuum-deposited PDMS film are repro-

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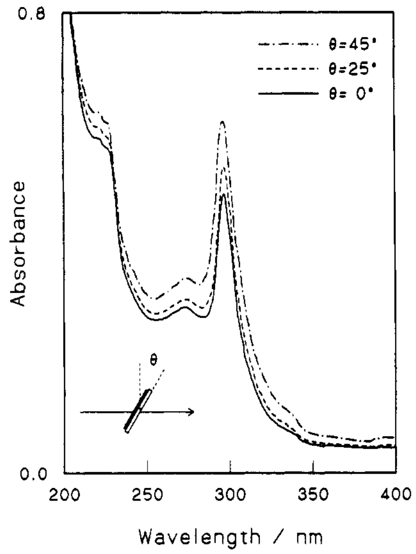

Figure 1. UV spectra of a vacuum-deposited PDMS film on a quartz plate at low temperature.

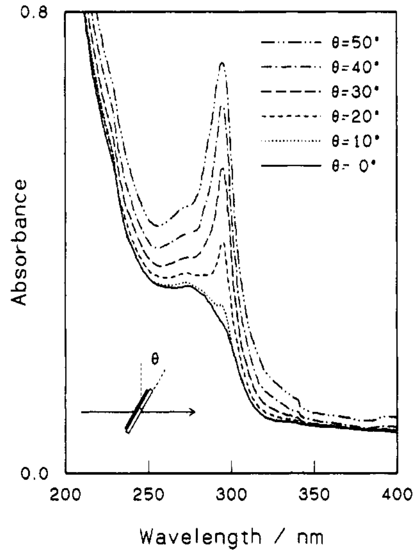

Figure 2. UV spectra of a vacuum-deposited PDMS film on a quartz plate at room temperature.

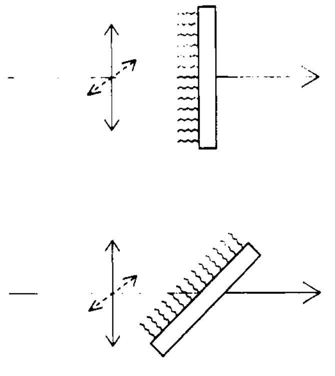

Figure 3. Schematic illustration of vacuum-deposited PDMS molecules.

duced in Figure 4 with solid and broken lines, which correspond to the polarized incident light shown by the solid and broken arrows in Figure 3, respectively. As expected, the 296 nm absorption was observed only in the spectrum measured by the polarized light shown by the solid arrow. This result also supports the interpretation that the PDMS molecules were oriented perpendicular to the substrate in the films deposited on the substrate at room temperature.

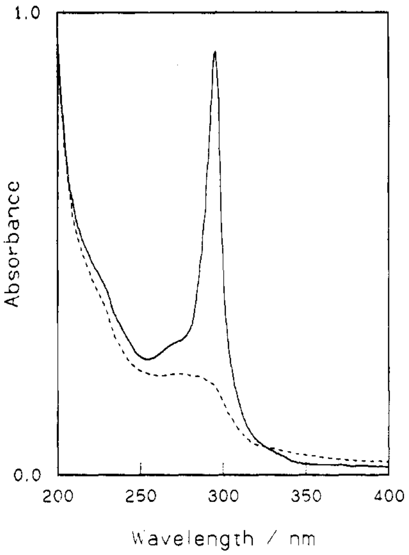

Figure 4. UV dichroism of an inclined (45°) vacuum-deposited PDMS film.

The cause of the difference in molecular orientation can be attributed to different temperatures of the substrates as follows. For PDMS molecules deposited on a substrate at low temperature, the vacuum-deposited molecules cool quickly and lose their mobility, and the molecules are randomly oriented in the film. On the other hand, the molecules deposited on a substrate at room temperature maintain a certain mobility after deposition. Then the molecules crystallize and orient in the film after the deposition, as has been found in some organic vacuum-deposited films.[19]

Thus, the behavior of the UV spectra of PDMS vacuum-deposited films with the inclined-sample alignments was explained in terms of the molecular orientation of the main chains of PDMS in vacuum-deposited films. The vacuum-deposition method could be one technique to make perpendicularly oriented polysilane films, in which the characteristic properties of polysilanes due to σ-electron delocalization are expected to appear specifically in the direction perpendicular to the film surface.

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